# TALLER INTERNACIONAL

## SOBRE ACTUALIZACION EN DESINFECCION DE AGUAS

ABRIL 25 AL 29 DE 1988
Cali - Colombia

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SECCIONAL VALLE DEL CAUCA

Sección Colombiana de AIDIS
A.A. 6720 Tels: 681075 - 671176
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**ORGANIZA:**
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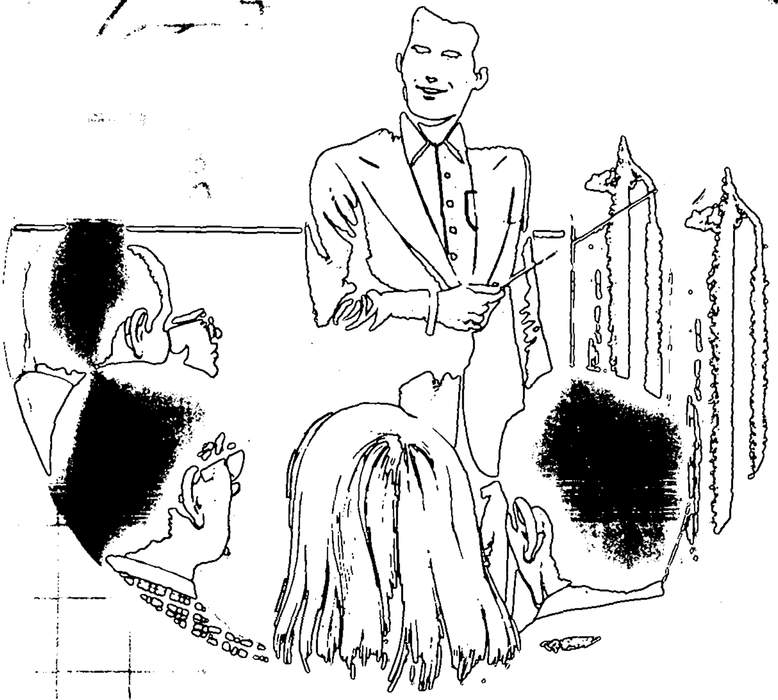

# MEMORIAS

# TALLER INTERNACIONAL SOBRE ACTUALIZACION EN DESINFECCION DE AGUAS

ABRIL 25 AL 29 DE 1988
CALI

## MEMORIAS

ASOCIACION COLOMBIANA DE INGENIERIA SANITARIA Y AMBIENTAL
ACODAL-SECCIONAL VALLE DEL CAUCA
SECCION COLOMBIANA DE AIDIS

APARTADO AEREO 6720 - TELEFONOS 671176 - 681075 - CALI - COLOMBIA

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# ACODAL-SECCIONAL VALLE DEL CAUCA

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# TALLER INTERNACIONAL SOBRE ACTUALIZACION EN DESINFECCION DE AGUAS

## CONTENIDO

Los siguientes temas se presentan en estas Memorias bajo autorización de su autor, Dr. Geo Clifford White.

# The Importance of the Disinfecting Process of Water for Human Use.

J. Edward Singley, Ph.D.

The history of the disinfection of water for human use dates back to the early days of history, even though the major need for such actions were minimal where the streams and rivers were relatively unpolluted by other human usage. The boiling of water for tea by the Chinese and the clarification of waters followed by transportation in silver vessels by Alexander the Great are early examples of such disinfection prior to any knowledge of the causes of water-borne illnesses.

The specter of vast plagues from polluted water haunted the Middle Ages in Europe and Asia. Cholera and typhoid fever decimated populations in major parts of the known world. Even today the developing and underdeveloped parts of the world are severely handicapped by the debilitation of the population by water-borne diseases. Schistosomiasis, giardiasis, intestinal parasites, and many other water-borne human pathogens have infected high percentages of the population in many areas. It was stated by President Martin Schalekamp at the International Water Supply Association meeting in Zurich in 1982 that over 50% of the hospital beds in the world are occupied by patients resulting from water-borne diseases. This is an astounding statistic when one considers the very small number of cases of water-borne diseases in the developed countries that require hospitalization. Even in the known cases the predominant cause has been the failure to provide adequate or continuous disinfection, although problems are encountered frequently in suppliers that are not disinfected by choice. This later option has led to several outbreaks within a historically uncontaminated well has been subjected to an unanticipated source of pathogens. Classic cases are the Riverside, California outbreak which infected about 18,000 residents with an enteric disease of unknown etiology and the Homestead, Florida migrant labor camp typhoid epidemic, which affected about 75 residents. Each case involved the lack of chlorination of a relatively shallow well.

The use of a disinfectant alone, though, may not be adequate to control pathogens. There are human pathogenic microorganisms that are relatively resistant to disinfection. Such a case is the recently identified organism <u>cryptospiridium</u>. It is highly resistant to . chlorine. Almost any pathogen is resistant when it can be sheltered by particulates. This is the reason that U.S. regulations require that a disinfectant be applied to low turbidity water.

There are many diseases of humans that are primarily conveyed to the affected individuals by ingested water. Thus, destruction or inactivation is essential for public water supplies. Among the diseases meeting this description are typhoid fever, schistosomiasis, giardiasis, hepatitis, amoebiasis, legionellosis, cholera and other as shown in Table 1.

The rest of this chapter is taken from an EPA report to Congress entitled "Comparative Health Effects Assessment Report," 1987, Chapter 3, written by Charles Gerba, Richard Bull and Rhodes Trussell.

## Risks from Waterborne Infectious Disease

### Impact of Waterborne Diseases on Human Health

Today, as throughout the history of civilization, microorganisms are the major cause of illness associated with the food and water we consume. In 1980 it was estimated that 25,000 people per day die from the consumption of contaminated water and that one hospital bed in four in the world is occupied by someone who became ill from polluted water (WHO, 1979). Perhaps 80% of all diseases in the world are related to contaminated water (WHO, 1979). It has been estimated that there are in the order of five billion waterborne infections each year in Africa, Asia and Latin America (Walsh and Warren, 1979). Food and waterborne disease is one of the major causes of diarrhea with up to one billion cases every year in children under five (World Health Organization, 1984). Diarrhea is a frequent cause of mortality in most of the developing world today (MMWR, 1983). The world wide impact of foodborne illnesses alone associated with microorganisms is estimated at $20 billion annually (Todd, 1987).

These statistics largely relate to the developing world where both the quality and quantity of drinking water is not equal to that available in the United States and the rest of the industrialized world. The incidence of disease agents commonly associated with waterborne transmission are now uncommon or far less prevalent in the United States today. Examples include typhoid, cholera and infectious hepatitis. While the incidence of disease caused by these microorganisms is low in the United States today, the potential contamination of drinking by these organisms always poses a risk to the population. Such agents can and often are present in natural waters used as raw sources for our drinking water supplies, and in some instances are present in relatively high concentrations (Berger and Argaman, 1983). In addition to traditional enteric pathogens there is now an awareness that microorganisms whose natural habit is in water may also cause disease in susceptible individuals. An example, is respiratory illness caused by Legionella bacteria which may grow in the water distribution system.

The epidemiology of waterborne pathogens is complex and drinking water treatment, while often a significant barrier to the spread of disease causing microorganisms, is only one and its relationship to other routes needs to be considered.

### 3.2.2 Epidemiology of Waterborne Microorganisms

Four major groups of water related infectious disease agents have been distinguished: (a) waterborne, (b) water-washed, (c) water-based, and (d) water-related insect vector-borne (Feachem et al., 1983). The first three groups are especially relevant to drinking water and the agents in Table 4-1 are in one or two of these three categories. Many of the potential drinking water pathogens are excreted or shed by infected humans and/or animals. These organisms may be transmitted by direct ingestion (waterborne), or contamination of food or skin. In any sizeable population, some people are likely to be infected with, and therefore excreting or shedding at least some of these potentially waterborne or water-washed agents. Waterbased disease organisms are those organisms naturally present in water such as the Legionella bacteria and certain parasites.

TABLE -1

## MICROORGANISMS PATHOGENIC TO MAN WHICH CAN BE TRANSMITTED BY WATER

| Group | Pathogen | Disease Caused |
|---|---|---|
| Bacteria | Salmonella (>2000 types) | Typhoid, paratyphoid, salmonellosis |
| | Shigella (4 spp.) | Bacillary dysentery |
| | Enteropathogenic Escherichia coli | Gastroenteritis |
| | Yersinia enterocolitica | Gastroenteritis |
| | Campylobacter jejuni | Gastroenteritis |
| | Vibrio cholerae | Cholera |
| | Leptospira | Well's disease |
| | Legionella pneumophila | Acute respiratory |
| Protozoa | Entamoeba histolytica | Amebic dysentery, liver abcess, colonic ulceration |
| | Giardia lamblia | Diarrhea, malabsorption |
| | Balantidium coli | Mild diarrhea, colonic ulceration |
| | Cryptosporidium | Diarrhea |
| | Naegleria flowleri | Meningoencephalitis |
| Helminths | Ascaris lumbrioceides (Roundworm) | Ascariasis |
| | Ancyclostoma duodenale (Hookworm) | Anemia |
| | Necator americanus (Hookworm) | Anemia |
| | Taenia saginata (Tapeworm) | Taeniasis |
| | Trichuris (Whipworm) | Abdominal pain, diarrhea |
| | Toxocara (Roundworm) | Fever, abdominal pain |
| | Strongyloides (Threadworm) | Abdominal pain, nausea, diarrhea |
| Enteroviruses | Poliovirus | Meningitis, paralysis, fever |
| | Echovirus | Meningitis, diarrhea, rash, fever respiratory disease |
| | Coxsackievirus A | Meningitis, herpangina, fever respiratory disease |
| | Coxsackievirus B | Myocarditis, congenital heart anomalies, pleurodynia, respiratory disease, fever, rash, meningitis |
| | New enteroviruses (Types 68-71) | Meningitis, encephalitis, acute hemorrhagic conjunctivitis, fever, respiratory disease |
| | Hepatitis Type A (Enterovirus 72) | Infectious hepatitis |
| | Norwalk virus | Diarrhea, vomiting, fever |
| | Calicivirus | Gastroenteritis |
| | Astrovirus | Gastroenteritis |
| | Reovirus | Not clearly established |
| | Rotavirus | Diarrhea, vomiting |
| | Adenovirus | Respiratory disease, eye infections gastroenteritis |
| | Snow-Mountain Agent | Gastroenteritis |
| | Epidemic non-A non-B hepatitis | Hepatitis |

The spread and thus the incidence of enteric microbial disease within a given community is related to a number of interacting factors (Table -2) which are a measure of the overall sanitation of the community. Studies have shown that improvements in any one of these factors will usually result in a reduction in prevalence of enteric illness (Esrey et al., 1985). However, improvements in water quality alone have not always had a measurable major impact on the spread of some enteric diseases. This is because enteric microorganisms may also be spread through the fecal-oral route by personal contact and contamination of inanimate objects and food. In addition, water availability (i.e. quantity) will also have an impact since this availability increases bathing, hand washing, food preparation, and the use of flush toilets which leads to overall improvement in the personal hygiene of the community. Improvements in drinking water quality in the United States (i.e. disinfection and filtration) had an immediately observable impact on the case of typhoid in the earlier part of this century probably because of already existing water availability and personal hygiene habits.

In developing countries the incidence of enteric disease and mortality from these diseases is high. Because of poor personal hygiene and water quality, and lack of adequate water supplies and disposal facilities exposure to these organisms occur early in life. Because of the early exposure the adult population has a generally lower incidence of disease because of the development of protective antibodies against the agents which tend to protect them from reinfection or acts to reduce the severity of recurrent

TABLE -2

## FACTORS CONTROLLING THE SPREAD OF ENTERIC MICROORGANISMS WITHIN A COMMUNITY

| |
|---|
| Personal Hygiene |
| Waste Disposal |
| Water Quantity |
| Water Quality |

disease In developed countries such as the United States the preexisting immunity of the population to many enteric microorganisms is significantly less and exposure via the drinking water results in an explosive outbreak in a community. Thus, the lower incidence of enteric disease by microorganisms in our environment may be attributed to our greater standard of living which acts to make the population more susceptible to disease via the ingestion of contaminated drinking water. This helps explain the often explosive nature and high attack rate observed during waterborne disease outbreaks in the United States today (Craun, 1986).

## Microorganisms Associated With Waterborne Disease

Enteric pathogens are those which are most commonly associated with waterborne disease in the United States. These organisms include bacteria, viruses, and parasites which are excreted in the feces of man and animals. Once excreted these organisms may survive for prolonged periods of time in water, even months to years under the proper environmental conditions (Feachem et al., 1983). Many survive conventional sewage treatment, particularly viruses and parasites, in concentrations capable of causing disease (Feachem et al., 1983). A summary of those pathogens of major concern which may be transmitted by water and the disease which they cause are shown in Table 3-1.

As a probable result of high standards of sanitation and water and wastewater treatment enjoyed in the United States, many of these pathogens, particularly the helmenths, are not a major problem, unlike the developing world where they are common.

Currently Giardia is the agent most commonly associated with waterborne disease outbreaks in the United States when an agent can be identified (Craun, 1986). Other documented agents of waterborne in the United States in recent decades include Cryptosporidium, hepatitis, Shigella, Salmonella, Campylobacter, Yersina, Norwalk virus and rotavirus (Craun, 1986). However, it should be remembered that in most outbreaks no agent or cause can be identified. Such outbreaks may be caused by agents for which no method is available for their detection or the failure to take samples for testing. It should also be recognized that new agents which can be potentially transmitted by water are discovered almost every year. In the case of enteric viruses almost two new agents have been discovered each year over the last decade and a half (Gerba, 1984) which could be transmitted by water. The list of potential waterborne disease agents is obviously larger than indicated in Table 3-1.

It should also be recognized that the list of pathogens and their relative significance is not constant. Microorganisms are continually evolving and new strains and types of organisms of greater or lesser virulence appear. One only has to be reminded of the recent emergence of human immuno-deficiency virus (AIDS). An example among the enteric viruses is enterovirus type 70 which is believed to have originated from an animal or insect virus in the mid 1960's and since caused a worldwide pandemic of hemorrhagic conjunctivitis among the human population in the developing world (Miyamora et al., 1986).

## Impact of Water Treatment on Waterborne Disease

Concomitant with the recognition and acceptance of drinking water as a significant route of infectious disease transmission was the introduction of filtration and disinfection processes. Disinfection in this country has always been synonymous with chlorination. The first continuous application of chlorine to disinfect a municipal water supply in the United States occurred in 1908 when sodium hypochlorite was used to disinfect the Boonton reservoir of Jersey City, N. J. (Craun, 1986). The early acceptance of chlorination as a public health safeguard provided for its rapid expansion. Perhaps the most widely recognized achievement of drinking water treatment in the United States has been the dramatic reduction in typhoid fever which in large part is attributed to this single public health measure (Akin et al., 1982). In 1900, the annual typhoid death rate in the United States was 36 per 100,000. As water treatment became more common the rate declined to 20 and 3 per 100,000 in 1910 and 1935, respectively (Akin et al., 1982).

The impact of water treatment on typhoid incidence in Philadelphia at the turn of the century is shown in Figure -1. In 1906 in Philadelphia, there were more than 9,000 cases of typhoid fever per year. After routine filtration of drinking water was introduced the number of cases per year had dropped to 1,000. Chlorination, which began in 1913, dropped the number of typhoid cases to less than 600 in 1914 and to less than 200 by the mid-1920's (Kilbourne and Smillie, 1969)

Perhaps one of the more dramatic examples of the benefits of disinfection was that of the observations in Wheeling, West

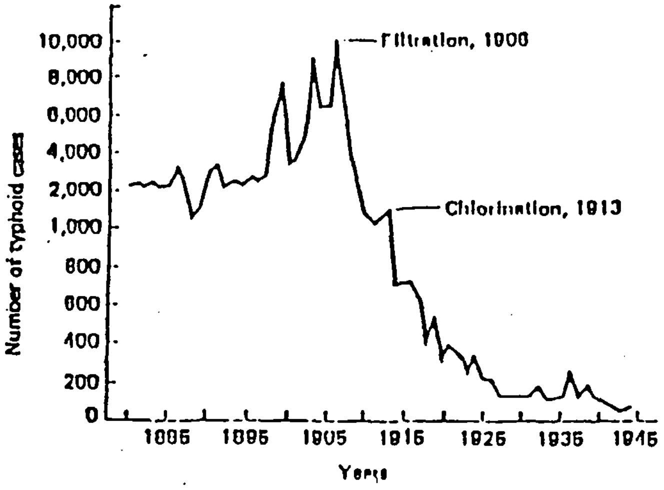

Figure 1. The dramatic effect of water purification on incidence of water-borne disease. The graph shows the incidence of typhoid fever in the city of Philadelphia during the early part of the twentieth century. Note the marked reduction in incidence of the disease after the introduction of filtration and chlorination. (Source: Brock, T.D., K.M. Brock and D.M. Ward. 1986 Basic Microbiology With Applications. 3rd. ed. Engelwood Cliffs, New Jersey, Prentice Hall.

Virginia as cited in the first volume of Drinking Water and Health (1977). The incidence of typhoid fever in Wheeling in 1917-1918 was 155-200 per 100,000. Chlorination was introduced in the latter part of 1918, with the result that during the first three months of 1919 only seven cases were recorded. During three weeks in 1919 chlorination was discontinued, and the number of cases increased 300%. Chlorination was continued thereafter, and only 11 cases were recorded for the remaining six months of the year.

The significance of water treatment today is illustrated by a recent study in Columbia where diarrhea illness rates were found to be inversely related to the measured level of free chlorine in the water supply (Bersh and Osoria, 1985). A recent review study to determine the effect of water quality on diarrhea illness (Esrey, 1985) concluded that diarrhea is reduced 27% and morbidity 30% with an improvement in water quality delivered to households.

While water treatment and disinfection may have dramatic impacts on the incidence of certain enteric diseases it should be recognized that such treatment will not necessarily eliminate the disease from the population. In addition, the impact for all enteric diseases may not be equal (Table -3). This is particularly true for enteric parasites and viruses which have a low infectious dose and are more resistant to inactivation and removal by water treatment processes. This may help explain why enteric viruses and parasites are the leading cause of cases of waterborne disease in the United States when an agent can be

## TABLE -3

## ESTIMATED REDUCTIONS IN WATERBORNE DISEASES IN RELATION TO IMPROVEMENTS TO WATER SUPPLIES

| Disease | Percentage Suggested Reduction by Water Improvements |
|---|---|
| Cholera | 90 |
| Typhoid | 80 |
| Leptospirosis | 80 |
| Viral hepatitis | 10 |
| Enteroviruses | 10 |
| Amoebic dysentery | 50 |
| Ascariasis | 40 |

* modified from Bradley (1977).

identified, as compared to years previous to 1971 when typhoid and shigellosis were the leading causes (Craun, 1986).

### 3.2.5 Waterborne Disease in the United States Today

A hundred years ago, before the advent of modern water treatment, diarrhea was a leading cause of death in the United States. Diseases associated with fecally contaminated food and water such as typhoid and cholera were common in the last century. The incidence of these pathogens in the United States declined dramatically during the early part of this century with the advent of drinking water disinfection and improved sewage treatment and disposal. For example, in the U.S. in 1908, 40% of the typhoid was transmitted via drinking water, compared to 1.4% between 1946 and 1964 (Cliver and Newman, 1984). Still the major documented cause of waterborne illness in the United States is microorganisms (Craun, 1986). Most outbreaks are believed due to the use of untreated water, systems receiving inadequate treatment or contaminated after treatment (Figure 3-2). Over half of the outbreaks were due to the use of non-disinfected or inadequately treated water. Outbreaks occur from the use of both surface and ground water, with almost half each year being due to contaminated groundwater (Figure 3-3). Between 1920 and 1983 there were 1,531 waterborne outbreaks reported in the United States (Craun, 1986). An etiologic agent was determined in 61% of these outbreaks. A microbial agent could be identified as a probable cause in 48% of the outbreaks and chemicals in 4%. The remaining outbreaks resulted in illness categorized as acute gastroenteritis characterized by symptoms including abdominal

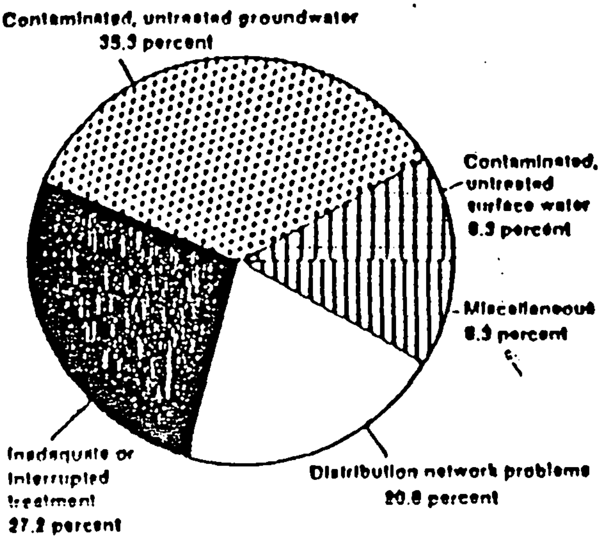

Figure 2. Waterborne disease .utbreaks by deficiency in public water systems. (Source: Lippy, E.C. and S.C. Waltrip. 1984. Waterborne Disease Outbreaks - 1946-1980: A thirty-five year perspective. <u>J. Amer. Water Works Assoc.</u> 76:60-67.

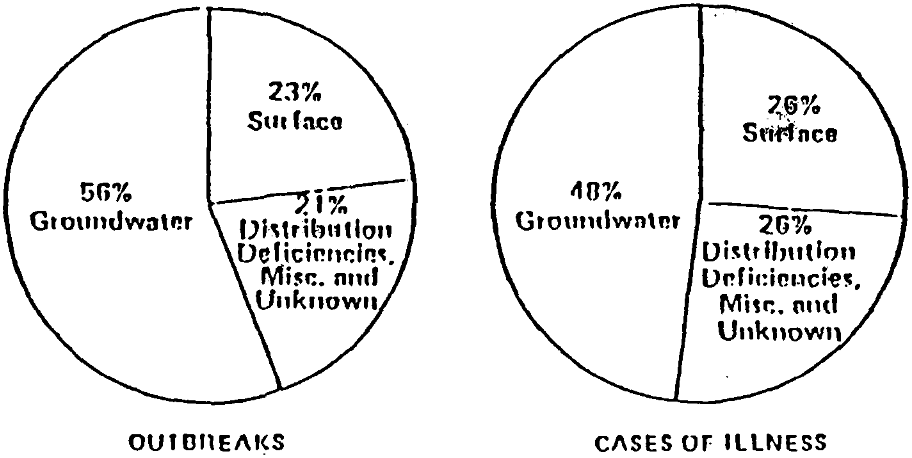

Figure -3. Waterborne disease outbreaks in the United States (1971-1977). (Source: Craun, G.F. 1979. Waterborne disease - a status report emphasizing outbreaks in groundwater. Groundwater 17:183-191.)

cramps, nausea, vomiting and diarrhea occurring 12 to 48 hours after consumption of the contaminated water (Craun, 1986). It is difficult to estimate how many of these outbreaks were caused by microorganisms, but not identified because clinical specimens were not collected or methods were unavailable for the isolation of the causitive organism. As methods for their detection have become available the number of outbreaks associated with parasites and viruses has increased (Craun, 1986; Rose and Gerba, 1986).

## Occurrence of Waterborne Disease Microorganisms in Untreated Water in the United States

The risk of acquiring a disease by water depends upon the occurrence and concentration of microbial pathogens in the water. Information on the actual occurrence of disease causing microorganisms in the United States is limited. This is because of the difficulty, cost, and lack of methods for the detection of many of these agents in water. Estimated concentrations of enteric pathogens in surface waters in the United States is shown in Table 4. The actual concentrations that might be present in water would be expected to vary greatly depending on the incidence of the disease in a community or animal population, time of year, sanitation within the community and other environmental factors. Because of the difficulty of isolating enteric pathogens from water coliform bacteria have been used to judge the sanitary quality and intensity of fecal contamination for over 70 years. Coliform and fecal coliform bacteria are common inhabitants of the gastrointestinal tract of all warm

## TABLE 4

## ESTIMATED LEVELS OF ENTERIC ORGANISMS IN SEWAGE AND POLLUTED SURFACE WATER IN THE UNITED STATES

| | Concentration (100 ml) in | |
|---|---|---|
| Organism | Raw Sewage | Polluted Stream Water |
| Coliforms | $10^9$ | $10^5$ |
| Enteric viruses | $10^2$ | $1-10^1$ |
| Giardia | $10^1$ | 0.1-1 |
| Cryptosporidium | $10-10^3$ | $0.1-10^2$ |

Source: Culp/Wesner/Culp. 1978 Guidance for planning the location of water supply intakes downstream from municipal wastewater treatment facilities. EPA Report, Office of Drinking Water. Washington, D.C.; Rose, J.B., D. Kayed, M.S. Madore, C.P. Gerba, M.J. Arrowood, C.R. Sterling and J.L. Riggs. 1987. Methods for the recovery of Giardia and Cryptosporidium from environmental waters and their comparative occurrence. Proceedings Calgary Giardia Conference, in press; Jakubowski, W. 1984. Detection of Giardia cysts in drinking water. Pp. 263-286 in Giardia and Giardiosis, Erlandsen, S.L. and Meyer, E.A. (eds.), New York: Plenum Press.

blooded animals and their presence in water is an indication of possible fecal contamination. Like enteric disease causing microorganisms they may gain entrance to surface waters from improperly treated sewage, human sewage, street runoff, feed lots and grazing lands in agricultural areas, and wildlife. Because surface waters are always exposed to human and animal activity these organisms are frequently isolated from surface water. Analysis of surface water quality data of the United States Geological Survey indicates that from 1975-1978 that surface water in much of the country exceeds 200 fecal coliforms/100 ml 50 to 99% of the time measurements were determined (Council on Environmental Quality, 1979). These data suggest that fecal contamination of natural surface waters and that disease agents can also be present in raw source waters.

Generally, groundwater from deep aquifiers is of good microbial quality, however this should not be taken for granted. Disease causing microorganisms, particularly viruses, may travel long distances in the subsurface under the proper conditions (Gerba and Bitton, 1984). A few extensive bacteriological surveys on ground water quality in the United States have been conducted and are summarized in Table 5. In these studies, 9 to 85% of the samples examined contained coliforms, and 2 to 75% of these same waters were positive for fecal coliforms. Enteric viruses are commonly isolated from groundwaters subject to contamination by domestic wastes (Keswick and Gerba, 1980) and groundwater is often associated with outbreaks of both viruses and parasites (Craun, 1986). Contamination of drinking water

TABLE -5

## MICROBIAL SURVEYS OF DRINKING WATER WELLS

| Survey | Number of Samples | Percent Positive for Coliforms | Percent Positive for Fecal Coliforms[a] | Reference |
|---|---|---|---|---|
| South Carolina rural supplies | 460 | 84.8 | 75 | Sandhu et al. (1979) |
| Colorado rural supplies | 164 | 41.3 | -- | Ford et al. (1980) |
| Community water supply study | 621 | 9.0 | 2.0 | Allen and Geldreich (1975) |
| Tennessee-Georgia rural water supplies | 1257 | 51.4 | 27.0 | Allen and Geldreich (1975) |
| Interstate highway drinking-water systems | 241 | 15.4 | 2.9 | Allen and Geldreich (1975) |
| Umatilla Indian Reservation | 498 | 35.9 | 9.0 | Allen and Geldreich (1975) |

[a] One or more organisms per 100 mL.

wells largely occurs in shallow wells or improperly sealed or placed wells. The degree of this contamination can be highly variable depending upon rainfall, natural of the soil and other environmental events (Gerba and Bitton, 1984).

In summary, the microbial quality of both surface and groundwater supplies cannot be taken for granted and are both subject to contamination by microbial pathogens.

## Effectiveness of Disinfection

All enteric pathogenic microorganisms are killed or inactivated by chlorine and other commonly used disinfectants used to treat drinking water. The amount of disinfectant required depends upon such factors as water pH, temperature, and turbidity. The type of organism is also important and viruses and parasites such as Giardia are more resistant than enteric bacterial pathogens (Table 6). Filtration of surface waters aids the removal of pathogenic organisms, particularly the parasites, and turbidity which interferes with disinfection. This treatment thus reduces the amount of disinfectant required but does not eliminate the need for disinfection. Current proposed guidelines for the control of waterborne disease outbreaks would require demonstrable 3 - 4 log removal of viruses of Giardia by any disinfection or filtration/disinfection processes (Regli, 1987). If this is implemented this will determine the future levels of disinfection in water supplies in the United States.

## TABLE 6

## UMMARY OF C-T VALUE RANGES FOR 99% INACTIVATION OF VARIOUS MICROORGANISMS BY DISINFECTANTS AT $5^{o}$ C

| Micro-Organism | Disinfectant |  |  |  |
|---|---|---|---|---|
|  | Free Chlorine pH 6 to 7 | Preformed Chloramine pH 8 to 9 | Chlorine Dioxide pH 6 to 7 | Ozone pH 6 to 7 |
| *E. coli* | 0.034-0.05 | 95-180 | 0.4-0.75 | 0.02 |
| Polio 1 | 1.1-2.5 | 768-3740 | 0.2-6.7 | 0.1-0.2 |
| Rotavirus | 0.01-0.05 | 3806-6476 | 0.2-2.1 | 0.006-0.06 |
| Phage $f_2$ | 0.08-0.18 | - | - | - |
| *G. lamblia* cysts | 47->150 | - | - | 0.5-0.6 |
| *G. muris* cysts | 30-630 | - | 7.2-18.5 | 1.8-2.0 |

Source: Hoff, 1986. Inactivation of Microbial Agents by Chemical Disinfectants. U. S. Environmental Protection Agency Report EPA/600/2-86/067, Cincinnati, Ohio.

### 3.2.8 Risks of Waterborne Illness from Untreated Drinking Water

Based on the most recently available outbreak data the risk of acquiring an illness from water in the United States is approximately $4 \times 10^{-5}$ per year or $2.8 \times 10^{-3}$ during a lifetime.* However, since there is no required reporting of waterborne disease outbreaks in the United States, the risk is probably greater since many outbreaks may go unreported (Craun, 1986). These risks are largely from the consumption of untreated drinking water. Risk from consumption of treated drinking water would be substantially less.

However, these risks are based on outbreak data only. Detectable outbreaks appear to only occur only when a water source is sufficiently contaminated to result in a significant number of cases as to be recognized by public health agencies as a common source outbreak. The impact of low levels of enteric pathogenic microorganisms in a water supply is more difficult to document. Infectious case studies with enteric viruses and parasites indicate that relatively low numbers of viruses and parasites, perhaps only 1 or 2 detectable units, are capable of causing infection (Ward and Akin, 1984; Rendtorff, 1954) acquiring an illness by this route. Constant exposure to hepatitis A virus at concentrations of one infectious unit per 10 liters or less would result in eventual exposure of every person consuming the water would eventually become ill with risk of

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* Based on an average of 9696 cases of illness between 1981-1983, population of 240,000,000 and 70 year lifetime.

mortality approaching that of the current mortality rate observed in the United States (Table 7). In the case of infectious hepatitis this is substantiated by the close association between antibodies to infectious hepatitis and sanitary conditions in various countries of the world (Frosner, 1984). Thus in developing countries the prevalence of antibodies against infectious hepatitis exceeds 80-90%. With such low infectious doses even small numbers of enteric pathogens in drinking water could potentially result in a significant risk of infection. Using available mortality data for enteric viruses and bacteria the risks infection, illness, and mortality to a susceptible population (i.e. no preexisting protective antibodies) from low levels in drinking water can be estimated (Gerba and Haas, 1986) (Figures 4 and 5). In the case of enteric viruses infection does not always result in clinical illness. These can be only broad estimates since the types and virulence of enteric organisms in a contaminated water supply would be expected to vary greatly over any lengthy period of time. However, such estimates serve to indicate that risks of consuming even low levels of pathogenic organisms could pose a significant risk of disease.

## TABLE 7

## MORTALITY RATES FOR ENTERIC BACTERIA AND ENTEROVIRUSES*

| Organism | | Mortality Rate (%) |
|---|---|---|
| *Salmonella* | | 0.2 |
| *Shigella* | | 0.13 |
| Hepatitis A | | 0.6 |
| Coxsackie | A2 | 0.5 |
| | A4 | 0.5 |
| | A9 | 0.26 |
| | A16 | 0.12 |
| Coxsackie B | | 0.59-0.94 |
| Echo | 6 | 0.29 |
| | 9 | 0.27 |
| Polio 1 | | 0.9 |

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* Source: Assaad, F. and I. Borecka. 1977. Nine-year study of WHO virus reports on fata viral infections. *Bull. Wld. Hlth. Org.* 55:445-453.; CDC (Centers for Disease Control). 1985. Hepatitis Surveillance. Report No. 49. CSD, Atlanta, Georgia; Berger, P. 1986. Letter dated June 4, 1986 to Charles P. Gerba.
Data for polio, coxsackie, and echo probably only represents hospitalized cases.

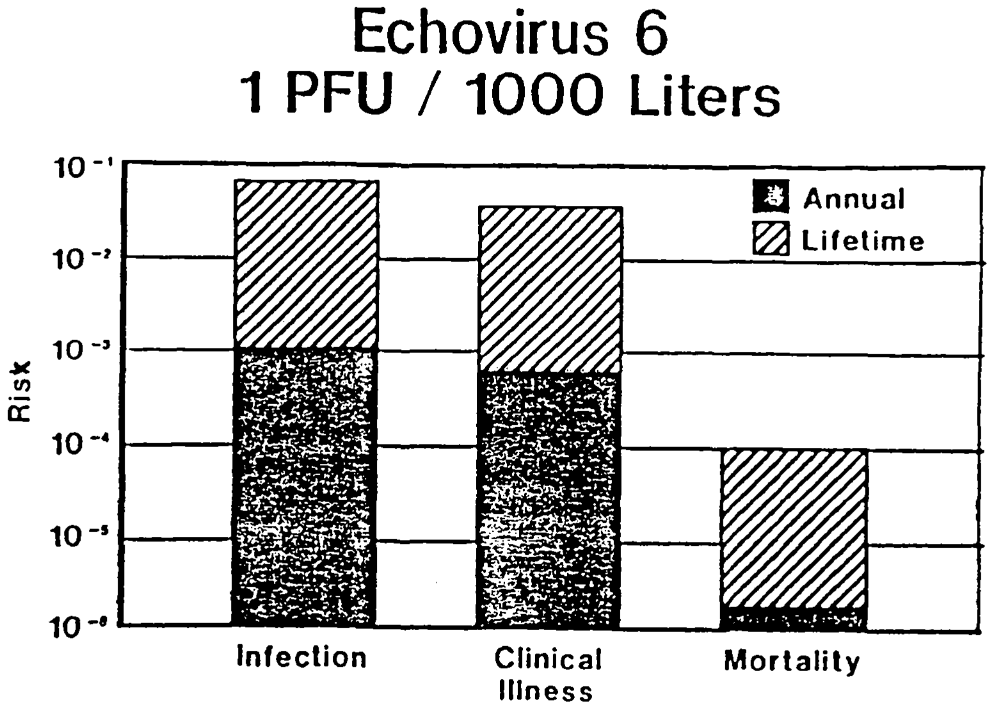

Figure 4. The estimated annual risk of infection, illness, and mortality from echovirus 6 assuming consumption of water containing one plaque form unit of virus (PFU) in 1000 liters. For the purpose of this risk analysis it was assumed that a person consumes two liters of drinking water per day. The minimum infectious dose data comes from Schiff et al. (1989) for echovirus 12, and a post-ingestion probability is assumed to have a beta distribution (Haas, 1983). Clinical illness rates are from Feign and Cherry (1981) and mortality from Table 3-7.

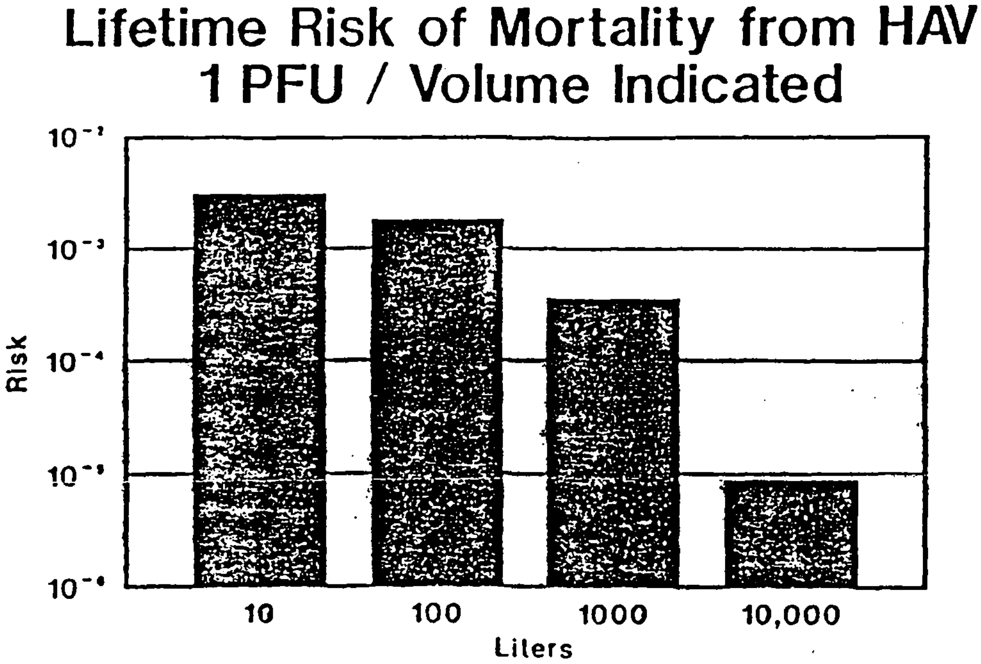

Figure 5. The estimated annual risk of infection, mortality of hepatitis A, assuming consumption of water containing one plaque form unit of virus (PFU) in the volume indicated. For the purpose of this risk analysis it was assumed that a person consumes two liters of drinking water per day. The minimum infectious dose data comes from Schiff et al. (1989) for echovirus 12, and a post-ingestion probablity is assumed to have a beta distribution (Haas, 1983). Mortality from Table 3-7.

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# METODOS QUIMICOS Y FISICOS DE DESINFECCION DEL AGUA

## VI. DISCUSSION OF DISINFECTANTS AND OXIDANTS

### A. BASIC ISSUES

The current interest in regulating disinfectants and disinfectant/oxidant by-products has been instigated by the recognition that when chlorine is added for disinfection purposes, it also produces halogenated organic materials. Their formation is a function of a number of factors, in particular the concentration and types of organic materials present in the water when chlorine is added, and the chlorinating conditions (amount of chlorine dosed, pH, temperature, reaction time, etc).

Therefore, the salient objective of water treatment now is to reduce the amounts of halogenated materials formed during the treatment process. In turn, this has prompted the three strategies identified by EPA:

1. Remove the undesired compounds after they have been produced;

2. Change disinfectants to those which do not produce the undesired by-products;

3. Reduce the concentrations of organics in the water before chlorine is added.

Modifications of these same three strategies also can be considered as applicable to coping with SOCs and their disinfection/oxidation by-products.

Of the three approaches, the first two can be criticized as disregarding the problem and treating the symptom ... keep the water treatment process the same, but either add processing to remove the undesired materials produced by water treatment, or switch to another disinfecting material which will not produce the undesired materials.

Only the third approach recognizes and treats the problem itself, that is, the concentration of organics in the water, and how to remove these "precursors" of undesired by-products or lower their concentrations before adding chlorine. If one assumes that technological logic will win the day over patchwork partial solutions, it can be expected that most water utilities will opt to apply the third strategy, provided that it is affordable.

#### 1. First Approach

Once the halogenated organics have been produced, they are very difficult and/or costly to remove from water. Oxidation is ineffective, even with ozone, for removal of THMs. Adsorption by

GAC is effective only for short periods of time, and GAC reactivation costs are quite high. Adsorption by powdered activated carbon (PAC) is costly and results in large quantities of sludge for disposal. Air stripping of volatile organic chemicals (VOCs) is efficient, but GAC may be required to adsorb the compounds (to prevent transfer of the pollutant from water to air), and the same problems of reactivation are present. Besides, after removal from the water, the VOCs now must be disposed of, and most of them will be subject to RCRA compliance under the appropriate hazardous waste disposal regulations.

### 2. Second Approach

Switching to an "alternative disinfectant" to chlorine (used as the primary and secondary disinfectant) is a logical approach, provided that the alternative disinfectant will:

(a) not produce halogenated organics,

(b) not produce other undesired disinfection by-products than those produced by chlorine,

(c) provide guarantees of microbial disinfection or inactivation at least equal to those provided by chlorine, and

(d) provide a stable residual disinfectant in the distribution system.

For economic reasons, most utilities also would like the alternative disinfectant to be no more expensive than chlorine. All of this, particularly the "same cost" requirement, is asking a great deal of any single candidate alternative disinfectant. Given the fact that chlorine has been applied as the disinfectant of choice throughout the world since the early 1900s, if a cheaper and better disinfectant were available, it should have been in commercial use by this time.

Candidate "alternative disinfectants" currently being considered by many water treatment specialists are: chlorine dioxide, monochloramine, iodine, ultraviolet radiation, and ozone. However, both ozone and UV radiation can be rejected as candidates because neither provides a stable residual level for distribution systems. Miller et al. (1978), after studying European and Canadian applications of ozone for disinfection, concluded that ozone can be used as the secondary, residual disinfectant, **but only if five conditions are met simultaneously:**

1. Water temperatures must be cool (to slow biological regrowths),

2. Water must be free of iron (to obviate growth of iron-consuming bacteria),

3. Water must be free of ammonia (to eliminate growth of nitrobacter microorganisms),

4. TOC values must be less than 1 mg/L (to minimize its use as food for microprocessing),

5. Residence time in the distribution system must be less than 12 hours (so that microbial regrowths will be minimal).

Even in France, where post-filtration ozonation for primary and some secondary disinfection has been practiced since the early 1900s, all five conditions were found by Miller et al. (1978) to co-exist only rarely.

Iodine can be rejected on the grounds that it collects in the thyroid gland of many humans, causing problems of public health concern to some people.

Chlorine dioxide can be used as the secondary disinfectant in distribution systems, and in the water treatment plant for the primary disinfection step. However, it must be realized that $ClO_2$ is reduced when it disinfects and/or oxidizes, producing some level of chlorite ion, $ClO_2^-$, from which chlorine dioxide is generated.

Chlorine dioxide produces hematological effects in both humans and laboratory animals (NAS, 1987, pp. 89-90). The mechanism of these effects is not known; however it is believed to be related to the oxidant properties of chlorine dioxide and its aqueous reaction products, chlorite and chlorate ions. In addition, thyroid and developmental neurological effects have been observed in laboratory animals. These thyroid effects are thought to be caused by its oxidation of dietary iodide ion in the gastrointestinal tract. The oxidized iodine then binds to either food or tissue, and is unavailable for absorption. The mechanisms of the neurological anomalies are unknown.

Because of this behavior, EPA currently recommends that the total oxidant levels $ClO_2$ usage (chlorine dioxide + chlorite ion + chlorate ion) should not exceed 1 mg/L. This means that usage of chlorine dioxide as the primary disinfectant must be limited to rather clean waters, requiring very low applied dosages.

In Germany, for example, $ClO_2$ is employed for distribution system residual at dosage levels not to exceed 0.3 mg/L (Miller et al, 1978). In Switzerland, restrictions on the use of $ClO_2$ are even more rigid, 0.15 mg/L being the maximum allowable dosage (Schalekamp, 1986).

In laboratory studies, Werdehoff and Singer (1986) have shown that the 1 mg/L total oxidants from chlorine dioxide will not be exceeded if the dosage of $ClO_2$ does not exceed 1.3 to 1.5 mg/L. This level has been confirmed in pilot plant and full-scale plant studies at Evansville, Indiana by Lykins and Griese (1986) (see Case History of Evansville, IN -- Section VIII.C.1).

By elimination, this appears to leave monochloramine as the only apparent candidate "ideal alternative disinfectant" to chlorine. On the other hand, monochloramine is a very much weaker disinfectant than chlorine (see Table IIA and Section VI.B on Technical Issues - Disinfection and Disinfectants). Because of the very high CT values of monochloramine for inactivating 99.9% of Giardia lamblia cysts and 99.99% inactivation of enteric viruses (see Table IIA), it is impractical to consider its use as a primary disinfectant for surface waters or groundwaters "directly influenced by surface water". Therefore, monochloramine should be considered only as the secondary disinfectant for these types of systems (U.S. EPA, 1987a,e).

### 3. **Third Approach**

Without much argument, except perhaps cost, the concept of reducing the concentration(s) of organics in water before chlorine is added will produce fewer halogenated organic DOBs. This approach addresses the basic problem of removal of organics. A more restrictive subset of this approach is to remove organics or lower their concentrations before any strong oxidant is added. This is because the oxidation products of disinfectants other than chlorine will not be well identified for some time ... perhaps never, since more sensitive analytical procedures and health effects data continue to be developed.

A compromise approach is to employ non-chlorinous oxidants in the early stages of water treatment (e.g., ozone, potassium permanganate, hydrogen peroxide, before or during rapid mix, and/or prior to filtration) to assist in the removal of organic materials by partial oxidation of the organics, more efficient flocculation and filtration. In such cases, the non-chlorinous oxidants do not produce halogenated oxidation products, except for those waters which may contain substantial amounts of bromide ion (which can be oxidized to hypobromous acid, which then may produce brominated organics, such as bromoform --- see Section VI.C, Technical Issues - Disinfection By-Products).

This third approach, although installed in many water treatment plants for the purpose of lowering the concentrations of disinfection/oxidation by-products, also is applicable to the simultaneous removal or reduction in concentration of many SOCs and VOCs.

## B. TECHNICAL ISSUES — DISINFECTION AND DISINFECTANTS

It is paramount that the disinfectant, applied for the purpose of disinfection (as opposed to being applied for oxidation) be capable of providing the required levels of microorganism kills or inactivations. In addition to reducing levels of total coliforms, heterotrophic plate count organisms, and legionella bacteria, disinfection currently is defined by EPA (U.S. EPA, 1987a) to mean a 99.9% reduction in Giardia lamblia cyst levels, and a 99.99% reduction in enteric virus concentrations.

### 1. For Systems Treating Surface Waters

#### a. The "CT" Value

Disinfection should be recognized as a [concentration x contact time] phenomenon (C x T product). That is, the weaker the disinfectant, the longer it must contact the water being disinfected. Therefore, one of the consequences of changing disinfectants will be the appropriate lengthening or shortening of the contact times, thus changing the sizes of disinfectant contact chambers.

In EPA's proposed Surface Water Treatment Rule (U.S. EPA, 1987a), several tables of CT values are provided as guidance for water treatment officials in coping with the microorganisms to be regulated (see Table I). Table IIA compares the CT values for the four major disinfectants over the pH range of 6 to 9 at 0.5°C to 25°C with respect to their abilities to achieve 99.9% inactivation of Giardia lamblia cysts: free chlorine (at 2 mg/L), ozone, chlorine dioxide, and preformed chloramines.

Several important conclusions can be drawn from Table IIA:

1. Ozone is by far the most efficient disinfectant of the four (CT values of 5 at 0.5°C to 1 at 25°C). This means that a 0.5 mg/L residual ozone concentration would have to be maintained over 10 minutes at 0.5°C ranging down to 2 minutes at 25°C in order to guarantee 99.9% inactivation of Giardia lamblia cysts.

2. Chlorine dioxide over the pH range of 6-9 is at least twice as effective as free chlorine at pH 6 only. At pH 7, 8, and 9, free chlorine becomes progressively less effective than chlorine dioxide.

3. A residual chlorine dioxide level of 1 mg/L would have to be maintained for 81 minutes at 0.5°C ranging down to 14 minutes at 25°C in order to guarantee 99.9% inactivation of Giardia lamblia cysts.

4. A residual of 2 mg/L of free chlorine at pH 7 would have to be maintained for 260 minutes at 0.5°C ranging down to 47 minutes at 25°C in order to guarantee 99.9% inactivation of Giardia lamblia cysts. If the water being disinfected also contains high trihalomethane formation potentials, using chlorine as the primary disinfectant under these conditions will produce high THM and other halogenated organic (see Table IV) concentrations.

5. When CT values are attained with free chlorine, chlorine dioxide, and ozone to inactivate 99.9% Giardia lamblia cysts, simultaneous attainment of 99.99% inactivation of enteric viruses is assured.

6. Preformed chloramines are by far the weakest disinfectant of all. To achieve 99.9% inactivation of Giardia lamblia cysts with a 2 mg/L residual would require contact times of 1,900 minutes at 0.5°C ranging down to 375 minutes at 25°C.

7. Much longer contact times are required with preformed chloramines to attain 99.99% inactivation of enteric viruses (CT values > 5,000 at 0.5-15°C) than to attain 99.9% inactivation of Giardia lamblia cysts. This means that attainment of the required 99.9% inactivation of Giardia lamblia cysts with preformed monochloramines **does not assure 99.99% inactivation of enteric viruses.**

This leads to the conclusion that surface water systems opting to use monochloramine as their primary disinfectant will have to demonstrate efficacy by conducting pilot scale tests with challenge organisms -- a costly and time-consuming process. Thus, from a practical and cost standpoint, monochloramine should not be considered as a primary disinfectant (U.S. EPA, 1987a;e).

### b. Suggested No Adverse Response Levels (SNARLs)

For substances not identified as known or suspected carcinogens and for which there are adequate toxicity data available from prolonged ingestion studies in humans or animals, the Subcommittee on Disinfectants and Disinfectant By-Products of the Safe Drinking Water Committee of the National Academy of Sciences has calculated Suggested No-Adverse-Effect-Levels (SNARLs). In a recent publication (National Academy of Sciences, 1987), SNARLs for adults and children are presented for chlorine dioxide, chlorite ion, chlorate ion, and monochloramine. These specific values are based on the assumption that 20% of the daily intake of these substances is by ingestion of drinking water, and are summarized in Table VI.

Also included in Table VI are recommended SNARLs for some of the 11 halogenated disinfection by-products listed by the EPA on July 8, 1987 for possible regulation.

### c. Possible Regulatory Consequences

Values for SNARLs recommended in Table VI are quite significant, by themselves, but also when considered in light of the CT values for the disinfectants listed in Table IIA. Considered by themselves, they are indications of possible MCLs (or at least MCLGs) which EPA may propose and promulgate in the future (i.e., when the Groundwater Treatment Rule is proposed in 1991). If these SNARL values do become the basis for the corresponding MCLs, it is also probable that EPA will set the MCLG and/or MCL to protect the 70-kg adult, because exposure times would be calculated over a human lifetime.

Table VI. NAS RECOMMENDED SNARLs FOR DISINFECTANTS AND DISINFECTANT BY-PRODUCTS (NAS, 1987)

| Disinfectant/By-Product | for 70-kg adult | for 10-kg child |
|---|---|---|
| Chlorine Dioxide | 0.21 mg/L | 0.06 mg/L |
| Chlorite & Chlorate Ions | 0.024 mg/L | 0.007 mg/L |
| Monochloramine | 0.581 mg/L | 0.166 mg/L |
| Dichloroacetic Acid | 0.41 mg/L | 0.120 mg/L |
| Trichloroacetic Acid | 0.175 mg/L | 0.050 mg/L |
| Dichloroacetonitrile | 0.056 mg/L * | ----- |
| Dibromoacetonitrile | 0.161 mg/L | 0.046 mg/L |
| 2,4-Dichlorophenol | 7 mg/L | 2 mg/L |

* The Subcommittee does not recommend this SNARL because of concern that DCAN may be carcinogenic.

In this event, a projected MCL of 0.21 mg/L for chlorine dioxide will eliminate this material from consideration as a primary disinfectant and will virtually eliminate it from consideration as a secondary disinfectant.

At the same time, a projected MCL of 0.581 mg/L for monochloramine will virtually eliminate this material from consideration as a primary disinfectant because of the excessive contact times which would be required to attain 99.9% and 99.99% inactivation of Giardia lamblia cysts and enteric viruses, respectively, at this concentration. For example, at 0.5°C, a contact time of 6,540 minutes (109 hours = 4.5 days) would be required to assure 99.9% inactivation of Giardia lamblia cysts. At 25°C, a contact time of 1,281 minutes (21.5 hours) would be required. To attain 99.99% inactivation of enteric viruses at 0.5-15°C would require a contact time with monochloramine of > 8,606 minutes (> 143 hours = > 2.4 days).

The hypothesized 0.581 mg/L MCL for monochloramine would not eliminate this material from consideration as a secondary disinfectant. Under the proposed Surface Water Treatment Rule, a residual (secondary) disinfectant level of not less than 0.2 mg/L must be present in more than 95% of the samples taken each month, throughout the distribution system. However, disinfectant residuals higher than 0.2 mg/L, for any disinfectant, are not required because of concern for disinfection by-products (U.S. EPA, 1987a).

Under these projected regulatory restrictions, the concept of a single "alternative disinfectant" disappears, to be superseded by the concept of "alternative disinfecting **systems**". Such alternative disinfecting systems would involve the use of a primary disinfectant (e.g., ozone, ultraviolet radiation) to be followed by a secondary (residual) disinfectant (e.g., chlorine) for the majority of cases.

For systems whose raw waters have very low THM formation potentials, or in which THMFP can be lowered appropriately prior to disinfection, then chlorine can continue to be both the primary and secondary disinfectant. However, the luxury of continued application of chlorine as the predisinfectant and as the primary and secondary disinfectant will be dictated by the future THM regulations, as well as future regulations for other halogenated organic by-products of chlorination (see next section).

### 1. EPA'S PERSPECTIVE ON RECOMMENDED NAS SNARLS

In the latest draft of the proposed SWTR (U.S. EPA, 1987a), EPA rejects the NAS assumption that only 20% of the daily exposure to chlorine dioxide and monochloramine comes from drinking water. EPA expects that exposure to these disinfectants from sources other than drinking water is expected to be minimal. Therefore, assuming that near 100% of exposure comes from drinking water, the relative SNARLs might be estimated as 1 mg/L for chlorine dioxide (including its oxidation/reduction products, chlorite and chlorate ions) and 2.5 mg/L for chloramine. This is the basis for EPA's current recommendations that concentrations of these two disinfectants do not exceed 1.0 and 2.5 mg/L, respectively.

It is also possible that EPA might apply a different uncertainty factor (1,000) than used by the NAS (100) in calculating SNARLs (actually MCLs) for chlorine dioxide, chlorite and chlorate ions, and monochloramine. The significance of this possibility is illustrated in the following example SNARL calculation for monochloramine:

$$\frac{8.3 \text{ mg/kg bw/day} \times 70 \text{ kg} \times 0.2}{100 \times 2 \text{ liters}} = 0.581 \text{ mg/L, or } 581 \text{ ug/L}$$

where:

8.3 mg/kg bw/day = dosage in mg/kg of body weight per day

70 kg = average adult weight

0.2 = 20% of total daily intake

100 = uncertainty factor

2 liters = daily adult water consumption

It can be seen that changing the estimate of percent of total intake from 0.2 to 1.0 multiplies the calculated SNARL by a factor of five. On the other hand, changing the uncertainty factor from 100 to 1,000, decreases the calculated SNARL by an order of magnitude (a factor of 10).

For example, using an uncertainty factor of 1,000, the NAS SNARL for $ClO_2$ for adults becomes 0.021. When this figure is multiplied by 5 (to correct for 100% daily exposure rather than 20% exposure), the SNARL becomes 0.105 mg/L. Similar calculations for monochloramine gives a revised projected SNARL of 0.29 mg/L.

To put these potential regulatory limits into perspective, the three possibilities discussed above are summarized in Table VII for chlorine dioxide, chlorite and chlorate ions, and monochloramine.

From this table, the range of highest and lowest potential MCL levels can be projected, Variations A and B. In the June 25, 1987 draft of the proposed SWTR, EPA has rejected the NAS-proposed values and is proposing values close to the higher (Variation A) levels. However, further health effects studies are in progress, and these issues are to be revisited by EPA in about a year. At that time, it is possible that the current recommended maximum levels for chlorine dioxide and monochloramine may be lowered.

TABLE VII. PROJECTED MCLs FOR CHLORINE DIOXIDE AND CHLORAMINE

| Disinfectant or By-Product | Projected MCLs Based on Variations in Adult SNARLs | | |
|---|---|---|---|
| | June 87 NAS[a] | Variation A[b] | Variation B[c] |
| chlorine dioxide | 0.21 mg/L | 1.05 mg/L | 0.105 mg/L |
| chlorite/chlorate ions | 0.024 mg/L | 0.12 mg/L | 0.012 mg/L |
| monochloramine | 0.581 mg/L | 2.9 mg/L | 0.29 mg/L |

a 20% daily exposure; uncertainty factor = 100. This number has been rejected by the EPA (U.S. EPA, 1987a).

b 100% daily exposure; uncertainty factor = 100

c 100% daily exposure; uncertainty factor = 1,000

Therefore, the following possibilities appear with respect to chlorine dioxide and monochloramine:

1. If an MCL for chlorine dioxide is set at 0.10 mg/L (Variation B), chlorine dioxide would be eliminated both as a primary and secondary disinfectant on the basis of EPA's requirement of maintaining a minimum of 0.2 mg/L residual throughout the distribution system.

2. An MCL for chlorite/chlorate ions at either the highest or lowest value given may eliminate chlorine dioxide from consideration as a primary disinfectant.

3. For monochloramine, an MCL of 2.9 mg/L (Variation A) will allow this material to be applied both as a primary and secondary disinfectant. In fact, EPA's current proposal (U.S. EPA, 1098a;e) is to allow a maximum of 2.5 mg/L.

   On the other hand, an MCL of 0.29 mg/L (Variation B) would eliminate monochloramine from consideration as a primary disinfectant, but would not eliminate monochloramine as a secondary disinfectant.

Under these assumptions of total human exposure from drinking water, chlorine dioxide currently can be considered for primary and secondary disinfection, within the constraints of the appropriate "CT values", and monochloramine can be considered as a secondary disinfectant. However, there is a strong probability that MCLs will be proposed by EPA in a year or so which will be lower than currently recommended levels, and which will reduce the practicality of both disinfectants as primary, and probably as secondary disinfectants as well.

### 2. For Systems Treating Groundwater

As pointed out earlier, many groundwater systems which do not now disinfect will be required so to do, but the Groundwater Treatment Rule will not be proposed by EPA until 1991. Since cysts normally are not present in groundwaters (except in those groundwaters "directly influenced by surface waters), requirements to inactivate these types of microorganisms are not expected. However the other microorganisms listed in Table I (total coliforms, pathogenic viruses, heterotrophic plate counts, and legionella organisms can be expected to be regulated. If viruses are regulated, the same 99.99% inactivation requirement can be expected.

#### a. "CT" Values and SNARLs

It can be anticipated that CT values similar to those given in the Surface Water Treatment Rule will apply to the various disinfectants, as well as the SNARLs and/or the resulting MCLs/MCLGs, and the requirement for maintenance of a 0.2 mg/L secondary disinfectant level in the distribution system. Therefore, the same reasoning discussed above with respect to chlorine dioxide, chlorite and chlorate ions, and monochloramine should apply to eliminate these materials from consideration as primary and secondary disinfectants.

#### b. Possible Regulatory Consequences

This reasoning leads to the same conclusions regarding disinfection of groundwater systems as for surface water systems: in the majority of systems, the application of a primary disinfectant (e.g., ozone, UV radiation) will be necessary, followed by a secondary disinfectant (e.g., chlorine) for the residual to be carried throughout the distribution system.

As before, the ability to use chlorine as both the primary and secondary disinfectant will rest on the future MCLs for THMs and for other by-products of chlorination to be proposed by EPA in 1990 or 1991.

Groundwater systems may face an additional complication, however, when they are required to disinfect. Those groundwaters which contain significant levels of iron and manganese will produce insoluble iron and manganese oxides when treated with ozone or chlorine. This will necessitate the addition of filters to remove oxidized insoluble materials. In addition, both ozonation and chlorination also may produce flocculated organics, and precipitate turbidity-causing particulates.

Formation of these types of insoluble materials will require secondary disinfection after filtration.

One major advantage of UV radiation as the primary disinfectant for groundwaters is that at appropriate applied energy levels, bacterial disinfection occurs readily, without extensive oxidation. Therefore, for groundwater systems with iron and manganese in their raw waters, use of UV radiation followed by secondary chlorination might be the least-cost alternative disinfecting system.

## C. TECHNICAL ISSUES — DISINFECTION/OXIDATION BY-PRODUCTS

Although to date, EPA is regulating only the four THMs as disinfection by-products, a fifth THM and 11 halogenated organics have been listed (U.S. EPA, 1987d) for possible regulation, along with the four disinfectants themselves and chlorite and chlorate ions, and ammonia.

Akin et al. (1987) describe the current EPA Health Effects Research Program dealing with compounds which have been identified as disinfection by-products and for which health effects data currently are being developed. All of those under current investigation are halogenated compounds which are listed in Tables IV and V.

The major technological issue in controlling current DOBs is how to reduce the concentrations of these halogenated organic materials without compromising microbiological safety. Some will add, "...and without producing other by-products which are as potentially toxic (or of public health concern) as those produced from chlorine". Still others will add, "... and at no increase in costs".

### 1. Non-Halogenated DOBs

As has been concluded in an earlier discussion, only chlorine and ozone (possibly UV radiation for groundwater) appear to be the major disinfectants of the future for public water supplies. Ozone is known to produce oxygenated materials as oxidation products. High energy UV radiation also can produce oxidation products, provided that appropriate dissolved oxygen and peroxide levels are present. What types of non-halogenated oxidation products are produced by ozone and/or UV radiation, and what is known of their toxicities? Are similar types of non-halogenated oxidized organic materials produced from the use of chlorine?

### a. **From Ozonation** (Rice & Gomez-Taylor, 1986)

Ozone generally is not reactive with saturated aliphatic hydrocarbon compounds. However, other types of aliphatic compounds, particularly olefins, are readily oxidized to unstable ozonides, peroxides, and hydroperoxide intermediates to form primarily aldehydes, ketones, and acids. A by-product of all organic oxidations with ozone is hydrogen peroxide. In the presence of additional ozone, however, the $H_2O_2$ is decomposed into hydroxyl free radicals, which are more powerful oxidizing agents than the ozone molecule itself. Hydroxyl radicals are rapidly destroyed by bicarbonate and carbonate ions, which comprise the natural alkalinity of raw waters.

Although ozone is capable of oxidizing many organic compounds completely to $CO_2$ and water, this conversion usually requires large doses of ozone (> 3 moles $O_3$/mole of organic compound) and long reaction times (sometimes hours). Under drinking water treatment plant ozonation conditions (1 to 5 mg/L applied ozone dosage; 5 to 20 minutes contact time), organic compounds usually are only partially oxidized. The oxidized organic materials are more polar, of lower molecular weight, more biodegradable, and usually more readily removed from solution by flocculation and filtration.

Oxalic acid (HOOC-COOH) is found commonly as a "final" oxidation product of many aliphatic, aromatic, and heterocyclic organic materials, because of its very slow rate of oxidation with ozone. Acetic acid is another "final" oxidation product which also is resistant to further oxidation, even with ozone.

Formic acid and formaldehyde also are formed during the later stages of ozone oxidation of many organic materials. However, these two by-products are readily oxidized to $CO_2$ and water, provided sufficient ozone is present in solution. Ozone oxidation rates of intermediate organic oxidation products usually are slower than the oxidation rates of the original compounds.

In a few instances, ozone oxidation products have been isolated which are more toxic than the original compounds. For example, ozonation of the pesticide heptachlor produces heptachlor epoxide, almost quantitatively. Heptachlor epoxide is quite stable to continued ozonation (Hoffman & Eichelsdörfer, 1971).

Parathion and malathion produce paraoxon and malaoxon, respectively, as initial oxidation products upon ozonation. Both of the oxons are more toxic than are the original thion pesticides. However, upon continued ozonation, the intermediate oxons continue to oxidize, producing innocuous final oxidation products (Laplanche et al., 1983).

Ozonation of phenol can produce resorcinol, which is a known THM precursor. This may explain the observations made by several groups that in following ozonation of some surface waters directly with chlorination, higher levels of THMs have been produced than by chlorination alone (Rice, 1980). In most cases, however, ozonation followed immediately by chlorination produces lower concentrations of THMs.

Infrequent finding of higher THM levels after ozonation and immediate chlorination has led to moving the initial ozonation point to the rapid mix or before, to allow flocculation of the more polar ozone oxidation products during filtration. Chlorination then follows at a later treatment stage. Under these conditions, lower THM levels always are found.

The National Academy of Sciences (1987) report (p. 67) notes that oxidation products of ozone (as well as non-chlorinated organic oxidation products from chlorine and chlorine dioxide) are similar to the organic compounds formed by natural oxidation processes. In other words, a surface water source such as a lake will be experiencing prebiological and chemical oxidative processes for months, perhaps longer, by processes which are similar in their chemistries to oxidation processes used in water treatment.

It is concluded by the National Academy of Sciences (1987, p. 195) that little is known about the types of by-products produced by ozonation of natural organics, and that well-conceived studies need to be conducted which will focus on the stable compounds expected from ozonation reactions with humic materials. Since saturated aldehydes (non-toxic) are well-known oxidation products of organic materials, it is suggested (NAS, 1987) that particular attention should be paid to the search for unsaturated aldehydes (some of which are known toxicants) and for hydroxyhydroperoxides.

However, unsaturated aldehydes, if formed during ozone oxidation, should oxidize rapidly at the double bond with ozone, thus destroying them.

Finally, the National Academy of Sciences (1987, p. 196) states:

> "Notwithstanding the fact that these studies need to be carried out, drinking water suppliers should not dismiss the possibility of using ozone as an alternative to chlorine and chloramines in water treatment. Ozone is an excellent disinfectant (although it must be used in combination with a secondary disinfectant to maintain a residual in the distribution system); ozone is an excellent oxidant for the various needs of water treatment; it does not form chlorinated by-products; and the admittedly inadequate studies now available

point to lower toxicities of ozonated water than of chlorinated water."

### b. From Chlorination

From the aqueous chlorination of various humic materials, Stevens et al. (1985) identified 98 specific organic compounds, including 47 discrete compounds containing chlorine and 51 discrete compounds that did not contain chlorine. Christman et al. (1980) showed that the products of chlorination of aquatic humic materials generally fall into three broad structural categories: non-chlorinated substituted aromatics, chlorinated straight chain acids, and non-chlorinated straight chain aliphatic acids.

Seeger et al. (1984) showed that at low chlorine doses, which are typical of those conditions currently found in drinking water treatment plants and their distribution systems, a large number of ring-chlorinated aromatic acids is obtained, in addition to the numerous nonchlorinated aromatic and aliphatic compounds identified by earlier investigators.

In reviewing the available literature on products isolated and identified from the treatment of humic and fulvic acids in aqueous solution with ozone, chlorine, chlorine dioxide, and potassium permanganate, Rice & Gomez-Taylor (1986) concluded that the non-chlorinated oxidation products formed by all four oxidizing agents are similar.

More recently, Stevens et al. (1987a,b,c) isolated nearly 200 discrete compounds from 10 operating water utilities practicing chlorine disinfection. Of those compounds which were positively identified, 31 are non-chlorinated, and are similar to those identified in other studies of ozonation of humic/fulvic acids.

Therefore, consideration of ozonation as a water treatment agent should not be postponed simply on the basis of the myriad of oxidation products which are formed. Many of the same compounds are formed during chlorination.

## D. COMPARISON OF DISINFECTANTS - OXIDANTS

### 1. General Considerations

The capability of one substance to oxidize another is measured by its Oxidation Potential, normally expressed in volts of electrical energy (referenced to the hydrogen electrode). The oxidation potential is a measure of the relative ease by which an atom, ion, molecule, or compound is able to lose electrons, thereby being converted to a higher state of oxidation. If the oxidation potential of substance A is higher than that of substance B, then substance B can be oxidized by substance A. Oxidation potentials of representative oxidants/disinfectants commonly used or encountered in water treatment are listed in Table VIII.

Table VIII. OXIDATION POTENTIALS OF WATER TREATMENT OXIDANTS[a]

| Species | | Oxidation Potential, Volts |
|---|---|---|
| hydroxyl free radical | $(OH)^{\cdot}$ | 2.80 |
| • ozone | $(O_3)$ | 2.07 |
| hydrogen peroxide | $(H_2O_2)$ | 1.76 |
| permanganate ion | $(MnO_4^-)$ | 1.68 |
| • hypochlorous acid | (HOCl) | 1.49 |
| • chlorine | $(Cl_2)$ | 1.36 |
| • hypobromous acid | (HOBr) | 1.33 |
| • bromine | $(Br_2)$ | 1.07 |
| hypoiodous acid | (HOI) | 0.99 |
| • chlorine dioxide | $(ClO_2)(aq)$ | 0.95 |
| • iodine | $(I_2)$ | 0.54 |
| oxygen | $(O_2)$ | 0.40 |

a Source: Handbook of Chemistry & Physics, CRC Press, Inc.

• excellent disinfecting agents

Although the relative position of an oxidant in Table VIII is indicative of its ability to oxidize other materials, it does not indicate how fast one material will be oxidized by another, nor how far toward completion the oxidation reaction will proceed. One cannot tell from oxidation potentials alone whether a specific organic compound will be oxidized completely (to $CO_2$ and water) or only to the first of several intermediate stages.

One significant fact can be learned from Table VIII, however, at this point. As has been discussed in earlier sections of this report, it is rare that organic compounds treated with an oxidant even as powerful as ozone will be converted totally to $CO_2$ and water, under conditions normally encountered in water treatment plants.

Therefore, no other commonly employed and less powerful water treatment oxidant (such as chlorine, bromine, chlorine dioxide, etc.), all of which have lower oxidation potentials than ozone, will oxidize an organic material completely to $CO_2$ and water if ozone will not.

All oxidants weaker than ozone will be less effective than ozone in converting organic compounds to carbon dioxide and water, and thus may produce higher quantities of partially oxidized organic materials under water treatment plant conditions. It is important, therefore, for the water treatment professional to understand the chemistry of the organic components of the particular water supply when considering the use of any oxidant in the processing.

When oxidizing agents are added to water supplies containing specific organic compounds as impurities, it is not sufficient simply to follow the reduction in concentration of that compound. Other parameters, specifically the total organic carbon (TOC), provide needed information. With chlorine, the TOX (total organic halogen) also is a necessary parameter. It is also desirable to know the products of oxidation of the organic impurity which is being treated by the oxidizing agent.

When a discrete organic compound is oxidized, it may be totally destroyed by oxidation, but without a decrease in TOC content, In this instance, the concentration of oxidation products may be as significant as the concentration of the original impurity.

It is also important not to attempt to relate the disinfection capability of a specific oxidant to its oxidation potential. Ozone is the most powerful oxidant listed in Table VIII, and it is also the best disinfectant (i.e., its CT values are less than for any other disinfectant for a given species of microorganism). However hydrogen peroxide and potassium permanganate, which follow ozone in Table VIII, are known to be poor disinfectants, while iodine and chlorine dioxide, which have oxidation potentials less than half that of ozone, are very good disinfectants.

Table VIII is useful to the water treatment specialist in understanding the degree of chemical transformation which can be expected when various oxidizing agents are used at various stages of the water treatment process.

Table IX lists data for the various disinfectants, comparing the dosages and contact times required for 99% inactivation of *Escherichia Coli*. Table X lists similar data for 99% inactivation of Poliovirus Type I.

TABLE IX. COMPARISON OF DISINFECTION PERFORMANCE TO E. COLI [a]

| Test Organism | Disinfecting Agent | Concentration mg/L | Contact Time, min | CxT[b] | pH | Temperature, °C |
|---|---|---|---|---|---|---|
| E. coli | HOCl | 0.1 | 0.4 | 0.04 | 6.0 | 5 |
| | $(OCl)^-$ | 1.0 | 0.92 | 0.92 | 10.0 | 5 |
| | $NH_2Cl$ | 1.0 | 175.0 | 175.0 | 9.0 | 5 |
| | ozone | 0.04 | 0.50 | 0.02 | 7.2 | 1 |
| | ozone | 0.0125 | 0.33 | 0.004 | 7.0 | 12 |
| | $ClO_2$ | 0.30 | 1.8 | 0.54 | 7.0 | 5 |
| | $ClO_2$ | 0.80 | 0.35 | 0.28 | 7.0 | 25 |
| | iodine | 1.3 | 1 | 1.3 | 6.5 | 2-5 |
| | iodine | 0.30 | 2 | 0.60 | 9.1 | 20-25 |
| | $H_2O_2$ | 90 | -360 | 32,400 | 6.5 | ambient |
| | $KMnO_4$ | 1 | 45 | 45 | 5.9 | [illegible] |
| | $KMnO_4$ | 16 | 25 | 400 | 9.2 | 20 |

[a] From Drinking Water and Health, Vol. 2 (Washington, DC: National Academy Press, 1980), Chapter 2.

[b] Concentration of disinfectant times contact time.

### 2. Chlorine

This material is an excellent disinfectant, an excellent chemical oxidant, but also an excellent chlorinating agent. Its production of THMs is well-known, but it also produces a wide variety of additional halogenated compounds. In addition, chlorine is known to produce significant quantities of non-halogenated oxidation products. Some of these, from humic and fulvic acids for example, are identical to those produced by potassium permanganate, ozone, and chlorine dioxide (Christman, et al., 1980).

On the positive side, chlorine provides a stable residual for the water distribution system, provided that the water is free of chlorine-demanding ammonia and organic materials.

TABLE X. COMPARISON OF DISINFECTION PERFORMANCE TO POLIOVIRUS TYPE I [a]

| Test Organism | Disinfecting Agent | Concentration mg/L | Contact Time, min | $CxT^b$ | pH | Temperature, °C |
|---|---|---|---|---|---|---|
| Poliovirus I | HOCl | 0.5 | 2.1 | 1.05 | 6.0 | 5 |
| | HOCl | 1.0 | 2.1 | 2.1 | 6.0 | 5 |
| | $(OCl)^-$ | 0.5 | 21 | 10.5 | 10.0 | 5 |
| | $(OCl)^-$ | 1.0 | 3.5 | 3.5 | 10.0 | 15 |
| | $NH_2Cl$ | 10 | 90 | 900 | 9.0 | 15 |
| | $NH_2Cl$ | 10 | 32 | 320 | 9.0 | 25 |
| | ozone | 0.042 | 10 | 0.42 | 7.0 | 25 |
| | ozone | <0.3 | 0.13 | <0.04 | 7.0 | 5 |
| | $ClO_2$ | 0.3 | 16.6 | 5.0 | 7.0 | 5 |
| | $ClO_2$ | 0.8 | 1.5 | 1.2 | 7.0 | 25 |
| | iodine | 1.25 | 39 | 49 | 6.0 | 25-27 |
| | iodine | 20 | 1.5 | 30 | 7.0 | 25-27 |

[a] From Drinking Water and Health, Vol. 2 (Washington, DC: National Academy Press, 1980), Chapter 2.

[b] Concentration of disinfectant times contact time.

### 3. Chlorine Dioxide

This chemical is a powerful oxidant and disinfectant. Because of its instability, it must be generated on-site, which can be considered a disadvantage. In its pure state, $ClO_2$ does not produce trihalomethanes in the presence of organic materials which do produce THMs with chlorine.

Some procedures for synthesizing chlorine dioxide from sodium chlorite and elemental chlorine involve the use of excess chlorine. Thus, in these instances, some free chlorine is present in the water, resulting in the production of some THMs. The more that $ClO_2$ can be synthesized without the need for excess chlorine, the lower the concentrations of THMs which will be produced by the excess chlorine.

One procedure for generating $ClO_2$ free of excess chlorine is by addition of mineral acid to solutions of sodium chlorite.

Although chlorine dioxide does not produce the variety of chlorinated organic materials as does chlorine, nevertheless, some organic compounds do form chlorinated oxidation products, although in much smaller quantities than from chlorine (Rice & Gomez-Taylor, 1986). Mostly, however, $ClO_2$ oxidation products of organic materials are non-chlorinated.

A major disadvantage of chlorine dioxide is that as it performs its oxidation or disinfection work, about half of it reverts back to the chlorite ion. Although all of the toxicological parameters of chlorite ion are as yet unknown, it is known to produce hematological effects (Condie, 1986). Consequently, EPA currently recommends that the total residual concentration of chlorine dioxide, chlorite ion and chlorate ion not exceed 1 mg/L in finished water because of concerns about hematopoietic and possibly thyroid effects (Cotruvo and Vogt, 1985).

### 4. Monochloramine

This material is synthesized at the water treatment plant by the reaction of elemental chlorine with ammonia in equimolar quantities by one of three procedures:

1. Ammonia can be added to water already containing chlorine,

2. Chlorine can be added to water already containing ammonia,

3. A preformed solution of monochloramine can be added to the process water.

Procedure #1:

If chlorine is first added to the water to be treated to attain disinfection over a specific period of time, a CT contribution toward disinfection from free chlorine will be attained. However, the longer the free chlorine residual is sustained, the more halogenated organic materials which are not desired will be produced during the disinfection contact time. Thus there will not be major benefit to the use of chloramine, in that instantaneous halogenated organic levels will be the same. However, addition of ammonia will insure that THMs and other halogenated organics will not continue to be generated after monochloramine has been formed. In this manner, TTHM (and other halogenated organic) levels can be held to their initial levels.

Procedure #2:

If ammonia is first added to the water, then chlorine, provided that very good mixing is available, none of the water should be exposed to significant concentrations of chlorine. This will lower concentrations of halogenated materials, but not necessarily guarantee disinfection since monochloramine now is the disinfectant.

In certain cases, however, this approach may be even less effective. When chlorine is added to waters which contain organic nitrogen materials, such as proteins and aminoacids, the chlorine reacts much more rapidly with the organo-nitrogen compounds to form organic N-chloramines than with free ammonia to form the inorganic monochloramine (Weil & Morris, 1949; Morris, 1967). In turn, the organic N-chloramines are even weaker disinfectants than is monochloramine.

Even worse, standard methods of analysis for monochloramine based on iodometry (i.e., DPD) do not distinguish between inorganic monochloramine and organic chloramines, because both oxidize iodide ion to iodine in the determination of "combined residual" chlorine (NAS, 1987, pp. 62-63).

Thus, a water utility with raw water containing organic nitrogenous materials which adds ammonia, then chlorine to produce "monochloramine" for primary disinfection may be seriously overestimating the ability of its treatment system to provide the desired degree of disinfection.

Procedure #3:

To be assured of producing the minimum quantities of chlorinated organics, the chlorine and ammonia can be mixed in organic-free water, and the monochloramine solution can be added to the water being treated. This approach "preforms" the chloramine. However, this approach produces minimal disinfection and also is subject to the same competition with organic nitrogen compounds as discussed above.

### a. Chloramine Summation

Because chloramine is a much weaker disinfectant than is free chlorine, or any of the other disinfectants, the contact time required to assure disinfection of any particular organism will be longer than with chlorine, chlorine dioxide, or with ozone.

In some cases, such as with patients who are on kidney dialysis machines, the ingestion of chloramine-containing water can be fatal. In municipalities using $ClNH_2$ as the terminal disinfectant, the utility generally advises local hospitals and health maintenance centers of the presence of monochloramine in their tap waters, and advises these institutions to employ distilled water for their dialysis patients.

As with chlorine dioxide, the use of monochloramine as a bacteriostat can follow post-filtration disinfection by means of ozone, for example, to provide minimum production of halogenated organics. Monochloramine is a very poor chemical oxidizing agent. However, it is known to dissociate slowly in water to produce small quantities of hypochlorous acid, which in turn produce traces of halogenated organic materials (Rice & Gomez-Taylor, 1986).

In assessing all currently known facts about monochloramine, the Subcommittee on Disinfectants and Disinfectant By-Products of the National Academy of Sciences' Safe Drinking Water Committee has recently stated (NAS, 1987, pp. 194-195):

> "Because it is a much weaker disinfectant than chlorine, chloramine must be used at higher concentrations and for longer periods of contact to achieve sufficient disinfection. Even with extended contact time and higher concentrations, however, chloramination is not recommended as a primary disinfectant, especially where virus or parasitic cyst contamination is potentially present."
>
> "Preformed monochloramine is undesirable as a primary disinfectant."
>
> "The use of marginal chlorination as a method of introducing chloramines into a water supply system is specifically **not recommended** because, along with depletion of chlorine to produce inorganic monochloramine, organic chloramines that have even lower efficacy as disinfectants are formed. Organic chloramines have also been implicated as major contributors to the mutagenicity of chlorinated drinking and natural waters."
>
> There are currently no suitable methods for fully quantifying the organic chloramine fraction in the presence of inorganic monochloramine. Until such methods are developed, utilities that handle water supplies containing high concentrations of organic nitrogen run the risk of overestimating the ability of their systems to maintain adequate disinfection."
>
> "When free chlorine is used as the primary disinfectant, an amount should be used that is sufficient to produce a slight residual of free chlorine above that

required to oxidize nitrogen, followed by addition of ammonia to form monochloramine and limit THM formation."

## 5. Ozone

### a. General Considerations

This gas also must be generated on site, at the water treatment plant, because it is too unstable to be stored for significant periods of time in cylinders. Additionally, it is only partially soluble in water (about 13 times the solubility of oxygen). Therefore, one key to its successful use is proper gas/liquid contacting. If all of the ozone generated is not solubilized and reacted with water constituents, the excess ozone present after contacting must be reused or destroyed, in order to prevent unnecessary exposure of plant operating personnel to this material.

Because the generation, application, and handling of ozone is so foreign to the classical water treatment processor in the USA, and because of the relatively high capital cost of ozone generation and application equipment, the acceptance of ozone in North America has been slow to develop, even though it is used abundantly in other countries of the world (Miller et al., 1978).

On the positive side, ozone is the most powerful disinfectant and oxidizing material which is available to the water processor. It kills or inactivates all organisms tested in shorter periods of time than does any other disinfectant/oxidant available (see Tables IIA, IIB, VIII - X).

Ozone cannot produce any halogenated organic materials, other than indirectly, e.g., by oxidation of bromide ion (if that material is present in raw waters being treated) followed by bromination of organic precursors.

Being a powerful oxidizing agent, ozone used in very low applied dosages is able to neutralize charges on colloidal particles, thus causing them to precipitate. In higher applied dosages, ozone is quick to oxidize organic materials, but usually only partially. In rare cases, organic matter can be converted quickly to $CO_2$ and water by ozone. However, under normal water treatment conditions (i.e., dosages of 1-5 mg/L of ozone and contact/reaction times of 5-15 minutes), most of the organic materials contained in water are only partially oxidized.

### b. Disinfection With Ozone

For purposes of disinfection, it is necessary to generate ozone, on-site, and apply the gas (normally air + 1-5% ozone) to the water to be disinfected (using an appropriate gas/liquid contacting device) for a length of time appropriate to provide the CT values given in Table IIA for 99.9% inactivation of Giardia lamblia cysts. In practice, dissolved ozone levels of approximately 0.4 to 0.5 mg/L are attained and maintained during the disinfection process. Ozone contact times in currently operating water treatment plants using ozone for bacterial disinfection and viral inactivation are a minimum of 10 minutes, and range up to 15-20 minutes.

EPA's proposed Surface Water Treatment Rule requires attainment of 99.9% inactivation of Giardia lamblia cysts. From Table IIA, the highest CT value for ozone is 5 (for water temperatures of 0.5°C). This means that for a dissolved ozone concentration of 0.5 mg/L, a maximum contact time of 10 minutes would be required at 0.5°C to attain the CT value of 5. This length of contact time is easily within the design capabilities of the technology, and would not produce unique consequential problems of design and installation of ozonation systems.

As will be discussed in the following subsections, ozone has many applications in drinking water treatment which require its oxidation capability, and which are entirely unrelated to its disinfection capabilities. On the other hand, whenever ozone is used for oxidative purposes, it is possible to attain primary disinfection simultaneously, for most oxidative applications of ozone. The simplest method of attaining simultaneous primary disinfection is to extend the contact time appropriate to attain the necessary CT value at the particular water temperature.

However, knowledge of the dissolved ozone concentration during oxidation also is critical to attainment of the appropriate CT value. In certain oxidative applications, specifically ozone oxidation of waters containing high levels of iron and manganese (groundwaters), and preozonation for microflocculation and turbidity control (surface waters), measurement of a dissolved ozone residual is inappropriate.

In the case or iron and manganese, the dark, precipitating oxides produced upon ozonation will interfere with measurement of dissolved ozone. In the case of microflocculation or turbidity control, the objective is to apply a very low dosage of ozone, which means that a measurable concentration of dissolved ozone may never be attained. In these cases, ozone disinfection would have to be provided as a separate treatment step, normally practiced after filtration.

However, in all other oxidative applications, it is not only possible, but actually feasible to design the ozone dosage and contact time so as to produce the CT values required in Tables IIA and IIB. In taking credit for ozone disinfection prior to filtration, attention must be paid to the raw water turbidity and total coliform levels. Successful attainment of both oxidation and primary disinfection before filtration means that only secondary disinfection will be required after filtration.

### c. Microflocculation

Ozone oxidation of humic/fulvic materials can proceed to a variety of endpoints. With low applied ozone dosages, oxidation occurs primarily on the pendant groupings without cleaving the high molecular weight humic/fulvic polymer chains.

Partially oxidized organic materials contain a plurality of polar, oxygen-containing groupings, which now allow ready combination with cationic flocculating agents. Consequently, ozone can be effective in aiding in the removal of organics when used in or before the rapid mix step, provided that ozone oxidation is followed by coagulation then conventional or direct filtration.

On the other hand, when larger amounts of ozone are applied to solutions of humic/fulvic acids, not only does the oxidation of pendant groupings occur, but also oxidative scission of the high molecular weight humic/fulvic polymer chains. This produces low molecular weight, polar compounds, which are not as easily flocculated with cationic flocculating agents.

Thus, for optimum application as a flocculation aid, low applied ozone dosages should be employed. German experience in the use of ozone for microflocculation shows that the ratio of ozone applied to DOC (dissolved organic carbon) should be in the range of 0.1 (mg/L of applied ozone to mg/L of DOC) (Sontheimer, 1985).

### d. Promotion of Biodegradability

These same partially oxidized organic materials also are more biodegradable, and advantage is taken of this behavior in many European water treatment plants. For example, slow sand filters remove organics from drinking water by operating in a biological mode. Preozonation of the water fed to the slow sand filters increases the biodegradability of organic materials, and makes the combined oxidation/filtration step more effective (Rachwal, et al., 1987).

In a similar manner, if GAC adsorption is required for removal of refractory organic materials, and if some or all of the organic materials can be partially oxidized by ozonation, then preozonation prior to GAC filtration can promote biological removal of the partially oxidized organic materials in the GAC medium. The adsorptive capacity of such Biological Activated Carbon filters thus can be restricted to the ozone-refractory organics, while the ozone-sensitive organics (partially oxidized) are converted to carbon dioxide and water biologically.

The consequences of not providing a biological treatment step after ozonation in the water treatment plant are biological regrowths in the distribution system, unless a sufficient level of secondary disinfectant is present. If the secondary disinfectant is chlorine, then it is important that sufficient removal of organics has occurred before the chlorine is added. Otherwise, chlorinated organics still can be produced, sometimes in higher quantities than without ozonation (Rice, 1980).

### e. By-Products of Ozonation

However, the partial oxidation of organic compounds has raised some concerns as to the possible toxicities of the intermediate oxidation products formed upon ozonation. In the majority of cases, these oxidation products are oxygen-containing derivatives of the original organic materials, mostly aldehydes, ketones, alcohols, and carboxylic acids. Ozone is quick to rupture many unsaturated linkages in organic molecules, producing aldehydes and ketones.

There are, however, a few organic compounds from which ozone has been shown to produce toxic oxidation products. For example, the pesticide heptachlor, although rapidly oxidized to "destruction" by ozone, produces heptachlorepoxide nearly quantitatively. This example illustrates the absolute necessity of knowing what specific compounds are present in the water being oxidized and/or disinfected, in order to determine appropriate pre- and/or post-treatment procedures to cope with these undesired oxidation products.

### f. Catalytic Ozonation

For many organic compounds refractory even to so strong an oxidizing agent as ozone, the simultaneous application of ultraviolet radiation or hydrogen peroxide along with the ozone can accelerate otherwise sluggish reaction rates significantly. Acceleration is brought about by catalytic formation of hydroxyl free radicals, which are stronger oxidizing agents than ozone itself.

### g. Ozone Oxidation of Bromide Ion

Ozone does not form halogenated organic compounds, unless bromide ion is present in the raw water. If bromide ion is present, hypobromous acid will be produced, which can form brominated organic materials:

$$Br^- + O_3 \text{ -----> } (OBr)^-$$

$$(OBr)^- + H^+ \text{ -----> } HOBr$$

If bromide ion is present in sufficient quantity to result in the formation of bromine-containing organics in quantities which exceed current or projected MCLs, either the bromide ion should be removed, or an alternate source of raw water should be utilized.

### h. Summation for Ozone

Because it is such a powerful oxidizing agent and disinfectant (the strongest available for water treatment) and does not form halogenated by-products (except when bromide ion is present), ozone is the most versatile oxidant/disinfectant for water treatment.

As an oxidizing agent, ozone is useful added in very small quantities for turbidity control and microflocculation. In higher applied dosages, ozone oxidizes many troublesome inorganic materials (iron, manganese, sulfide, nitrite, arsenic), and destroys or alters the chemical structures of many organics responsible for tastes and odors, colors, THM formation, and other precursors of halogenated organics. Such alteration of chemical structures can make the oxidized organic materials readily removable from the treated water by flocculation/filtration, and/or by biological means. Many of the compounds listed as Synthetic Organic Chemicals by the EPA are at least partially oxidizable by ozone, although at varying reaction rates.

The more refractory, halogenated, organics which may be present in the raw water, which may not be oxidized with ozone at a practical rate, can be oxidized at greatly increased rates by combining ozone with UV radiation or with hydrogen peroxide.

The recent National Academy of Sciences Report (NAS, 1987, pp. 195-196) summarizes the latest thinking of the Subcommittee on Disinfectants and Disinfectant By-Products of the NAS Safe Drinking Water Committee with respect to water treatment and ozonation in particular as follows:

> "When possible, organic precursors should be removed prior to the disinfection process. This can be achieved by changing the order of the procedures of conventional treatment. A better approach, however, is to improve specific conventional treatment processes to remove organic compounds and to add processes such as carbon adsorption **and preoxidation.** Initial removal of organic by-product precursors precludes the need for reducing contact time, thus improving the efficacy of the disinfection processes and minimizing formation of organic chlorine by-products."
>
> The use of alternative oxidants, especially ozone and chlorine dioxide, will increase in the United States in the coming decades. Little is known about the types of by-products produced by ozonation of natural organics. Well-conceived studies need to be conducted that will focus on the stable compounds expected from ozone reactions with humic material. ... Particular attention should be given to the search for unsaturated aldehydes and the hydroxy-hydroperoxides."
>
> "Following these studies, further health effects studies are needed to determine whether ozone by-products are mutagenic or carcinogenic or produce other adverse effects. These studies should take into account variations that are likely to occur when the oxidation process is carried out in different matrices (pH, $O_3$/TOC ratio, alkalinity)."
>
> "Notwithstanding the fact that these studies need to be carried out, drinking water suppliers should not dismiss the possibility of using ozone as an alternative to chlorine and chloramines in water treatment. Ozone is an excellent (primary) disinfectant (although it must be used in combination with a secondary disinfectant to maintain a residual in the distribution system); ozone is an excellent oxidant for the various needs of water treatment; it does not form chlorinated by-products; and the admittedly inadequate studies now available point to lower toxicities of ozonated water than of chlorinated water."

### 6. Ultraviolet Radiation for Groundwaters

The effectiveness of ultraviolet radiation as a bactericide and virucide has been well established (U.S. EPA, 1986), but is not appropriate for the inactivation of Giardia lamblia cysts (Rice & Hoff, 1981). It is a physical disinfecting agent compared to the other disinfecting agents being used, whose actions are chemical. Radiation at a wavelength of 254 nm penetrates the microorganism cell wall and is absorbed by the cellular nucleic acids. This can prevent replication (reproduction) and cause death of the cell. Since UV radiation is not a chemical agent, no potentially toxic residuals are produced. Although the structures of certain chemical compounds may be altered by the UV radiation, the energy levels used for disinfection are too low for this possibility to be a significant cause for concern.

UV radiation at wavelengths of 254 nm is readily available commercially in standard equipment, available from a number of suppliers. It was reported (Angehrn, 1984) that in 1984, some 2,000 communities in Western Europe now disinfect their drinking water supplies by means of UV radiation.

Major advantages of UV disinfection are its simplicity, lack of impact on the environment, and minimal space requirements. There is a negligible likelihood of producing harmful chemicals in the water. Required contact times are very short, on the order of seconds rather than minutes. The equipment is simple to operate and maintain, but fouling of the quartz sleeves or Teflon tubes (housing the UV bulbs) must be dealt with on a regular basis. Fouling of these items normally is controlled by mechanical, sonic, or chemical cleaning.

Waters containing high suspended solids concentrations, color, turbidity, and soluble organic matter can react with or absorb the UV radiation, thus reducing the disinfection performance.

The major operating costs are power consumption and annual replacement of the UV lamps. Increased popularity and lowered costs have occurred due to improvements in modern lamp and system designs, increased competition, and improved reliability and simplicity of operation.

The biocidal properties of UV radiation make it a candidate for use as a primary disinfectant, which must be followed by a secondary disinfectant since UV radiation provides no disinfecting residual. In addition, at biocidal wavelengths (254 nm) and energies, UV radiation does not produce much oxidation of organic materials. However, at higher energy intensities and low UV wavelengths (i.e., 184.9 nm), oxidation of organic materials can occur readily to produce $CO_2$ and water.

The UV light spectrum is broad enough to include wavelengths of unequal effects upon different organisms. Even for efficacious wavelengths, the influence of the UV radiation may differ. Also, the devices designed to discharge UV light are not all alike in the radiant energy they generate. Moreover, the UV emanations are susceptible to absorption by the molecules of the organism-suspending medium. Their germicidal influence may be reduced by the time they reach the microbe.

That UV radiation is of practical utility in controlling most organisms is beyond challenge. The devising of effective UV systems requires being engineered, however. More than an ultraviolet radiation source is needed. Finally, where the organisms are killed by the UV radiation, subsequent removal of the dead microbes may be required, as by filtration, when the presence of particles is undesired, or when their catabolic products may manifest total organic carbon (TOC) levels, or pyrogenic lipopolysaccharides.

### 7. **Iodine**

Although iodine is not known to be used by any public water supply utility at present, it has been used on small scale to disinfect water during emergency situations. Iodine is known to concentrate in the human thyroid, and produce discomfort for certain groups of humans. Consequently, its use probably will continue to be restricted to emergency situations, with only minimal quantities being recommended.

## VII. DISCUSSION OF TREATMENT TECHNOLOGIES FOR DISINFECTION AND TO MINIMIZE PRODUCTION OF DOBs

### A. THE PROBLEM

In providing disinfection under the projected EPA drinking water regulations, water treatment systems will be faced with the challenge of how to disinfect surface and groundwaters to:

1. assure 99.9% and 99.99% inactivation of Giardia lamblia cysts and enteric viruses, respectively,

2. assure control of other microorganisms,

3. not impart toxicity to the disinfected water (mutagenicity, carcinogenicity, etc.),

4. minimize formation of chlorination and other undesired disinfection by-products, and

5. do all this without exceeding the projected MCL levels for the candidate disinfectants.

### B. THE STRATEGIES

Before disinfection is practiced, the attainment of two conditions is important:

1. turbidity levels should be reduced to 0.5 NTU or below, and
2. concentrations of organic materials should be as low as practicable, so as to minimize the production of oxidation and/or halogenation by-products.

If the raw groundwater has the appropriate levels of turbidity and concentrations of dissolved organics, pretreatment can be eliminated. Otherwise, at least filtration must be applied.

Concentrations of dissolved organics can be reduced by applying conventional treatments of flocculation, perhaps sedimentation, then filtration. Newer techniques of coping with organics concentrations include oxidation (before filtration, with ozone, potassium permanganate) and adsorption (powdered or granular activated carbon).

An emerging oxidation technology is the use of ozone coupled simultaneously with UV radiation or with hydrogen peroxide. This technique generates hydroxyl free radicals, which are more powerful oxidizing agents than ozone alone.

## C. DISINFECTION TECHNOLOGIES

According to the reasoning given earlier in this document, the use of chlorine for pretreatment and primary disinfection should be minimized. Reduction in the current 100 ug/L MCL for THMs is expected to be lowered by at least 50%. In addition, regulation of the 11 halogenated by-products of chlorination listed in Table III may place even greater restrictions on the use of chlorine for some utilities.

Projected MCLs for chlorine dioxide and its decomposition products (chlorite and chlorate ions) effectively eliminate this material as a primary disinfectant, except for very clean waters and/or short distribution systems.

The known limited capability of monochloramine to achieve the mandated percent inactivations of Giardia lamblia and enteric viruses eliminate this material from the role of primary disinfectant.

Therefore, for surface water treatment, only two primary disinfectants remain: chlorine and ozone. For groundwater, the same two primary disinfectants remain, plus UV radiation. For secondary (residual) disinfection, chlorine remains as the most viable, with occasional use of chlorine dioxide and monochloramine. The conditions of chloramination should be those recommended by the National Academy of Sciences (NAS, 1987): chlorination to the nitrogen breakpoint, followed by addition of ammonia.

Each disinfection approach will be discussed in this section. Much of this discussion is adapted from an earlier EPA publication (U.S. EPA, 1983) and supplemented by a more recent publication (U.S. EPA, 1986) which is a design manual for disinfection of wastewaters by means of chlorination, ozonation and UV radiation. Nearly all of the factors appropriate to disinfection of wastewaters is directly applicable to drinking water disinfection as well. Since most of the utilities which will be affected by the upcoming Surface Water and Groundwater Treatment Rules serve less than 10,000 persons, the emphasis of this discussion will be on the smaller utilities.

## 1. Primary Disinfectants

### a. Chlorine

Chlorine, symbolized chemically as $Cl_2$, is the disinfectant most commonly used by U.S. water utilities. It is available in three forms:

| Form | Formula | Name |
|---|---|---|
| gas | $Cl_2$ | chlorine gas |
| solid | $Ca(OCl)_2$ | calcium hypochlorite |
| aqueous solution | NaOCl | sodium hypochlorite |

The gaseous form is used most frequently, especially by larger water utilities, because it is the lowest cost form of chlorine.

#### i. Chemistry of Chlorination

In the gaseous form, chlorine will react with water to form hydrochloric acid and hypochlorous acid:

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{H_2O} \longleftrightarrow \underset{\text{hydrochloric acid}}{HCl} + \underset{\text{hypochlorous acid}}{HOCl}$$

The hypochlorous acid then will react with the water by dissociation to an extent determined by the pH of the solution:

$$\underset{\text{hypochlorous acid}}{HOCl} \longleftrightarrow \underset{\text{hypochlorite ion}}{(OCl)^-} + \underset{\text{hydrogen ion}}{H^+}$$

pH is a measure of the concentration of hydrogen ion in the water. The more hydrogen ion present, the lower is the pH. Conversely, the lower the hydrogen ion concentration, the higher will be the pH value.

At neutral pH (pH = 7.0), almost 80% of the chlorine is present in its most effective disinfecting form, hypochlorous acid; the remainder exists in the less effective hypochlorite ion form. As the pH increases, however, an increasing amount of HOCl will react with water to form more hypochlorite ion. At pH 8.0, for example, almost 80% of the chlorine present exists as the hypochlorite ion, almost a complete reversal of the situation which exists at pH 7.

From the CT data given in Table IIA for chlorine inactivation of Giardia lamblia cysts, it can be seen that the CT values for a 2 mg/L concentration of chlorine decrease rapidly for each temperature as the pH rises above 7.0.

Consequently, effective pH control is essential in order to guarantee the amount of disinfection designed in chlorination systems. Figure 1 shows the relationship between pH and the concentration of hypochlorous acid, the desired chlorine species in aqueous solution at 0°C and 20°C.

When the chlorination step is conducted by adding either sodium hypochlorite or calcium hypochlorite, the chemical reactions which occur result in an alkaline (basic) product as compared to the acidic product obtained when using the gas:

$$\underset{\text{sodium hypochlorite}}{NaOCl} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{hypochlorous acid}}{HOCl} + \underset{\text{sodium hydroxide}}{NaOH}$$

$$\underset{\text{calcium hypochlorite}}{Ca(OCl)_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{hypochlorous acid}}{2HOCl} + \underset{\text{calcium hydroxide}}{Ca(OH)_2}$$

The resulting hydroxides increase the pH values of the aqueous solutions. Since an increase in pH results in lower concentrations of HOCl, and therefore, poorer disinfection (requiring much longer contact times to provide the CT value to guarantee 99.9% inactivation of Giardia lamblia cysts and 99.99% inactivation of enteric viruses), the ability to adjust and control pH is critically important when using the hypochlorite forms of chlorine.

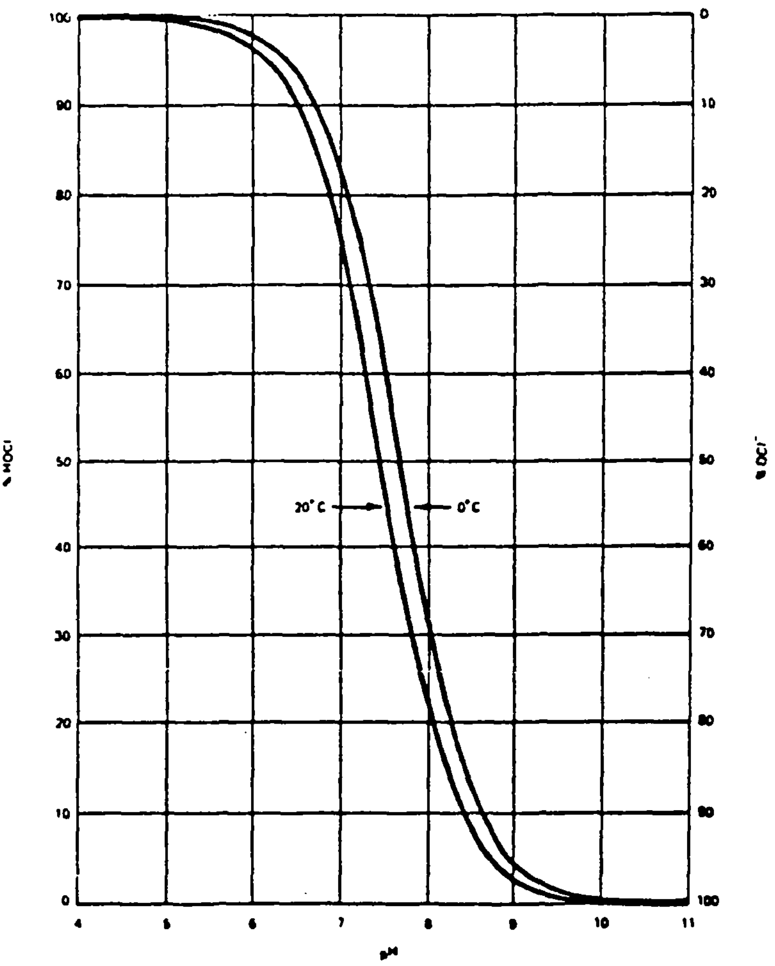

Figure 1. Distribution of hypochlorous acid and hypochlorite ions in water at different pH values and temperatures of 0°C and 20°C (AWWA, 1973).

### ii. Establishing A Chlorine Residual

Hypochlorous acid is one of the most powerful oxidizing agents known. This means that it will react with many substances present in the water being disinfected, in addition to the target organisms. This fact is clear from the known production of trihalomethanes, and many of the halogenated compounds listed in Tables III and IV.

In order to achieve a concentration of chlorine sufficient to guarantee the required level of disinfection. it is necessary to add enough chlorine to react with all of the reactive substances which are likely to be present, and then provide the excess "residual" chlorine. These reactions consume chlorine and are collectively called the "chlorine demand" of the water. Thus the chlorine demand of a water must be satisfied before a residual of free chlorine can be provided and an adequate job of disinfection can be attained.

The concentration of chlorine determined by an analytical procedure is called the "available chlorine residual", and it means only that amount of chlorine originally added which remains available for the disinfection operation. This residual may be either a free available residual or a combined available residual, or a combination of the two. Free available chlorine is essentially the sum of concentrations of hypochlorous acid and hypochlorite ions. Combined available chlorine is the sum of the concentrations of mono- and di-chloramines, plus nitrogen trichloride and organic nitrogen chlorine-containing compounds (see later discussion of Chloramines -- Section VII.C.2.b).

Intuitively, one would expect that each mg/L of chlorine added to water would be measurable as hypochlorous acid or hypochlorite ion. This is not the case, because chlorine reacts with many substances present in the water in complex manners.

To understand some of these complex reactions better, Figure 2 shows what is called a "breakpoint curve". The amount of chlorine added is shown on the horizontal scale and the amount of available chlorine determined by an analytical procedure is shown on the vertical scale.

Assume that the chlorine is added slowly and that the water contains small amount of reduced substances such as sulfides, ferrous iron, organic materials, organic nitrogen materials (aminoacids and proteins), and some ammonia, all of which exert a chlorine demand. The initial amount of chlorine added will be taken up by reactions with the reduced substances, and the analysis for free available chlorine [$HOCl + (OCl)^-$] will show that none is present.

After the chlorine demands of the reduced substances have been satisfied, then the HOCl will react with ammonia, organic nitrogen materials, and some of the organics present to yield chloramines and chlorinated organic compounds.

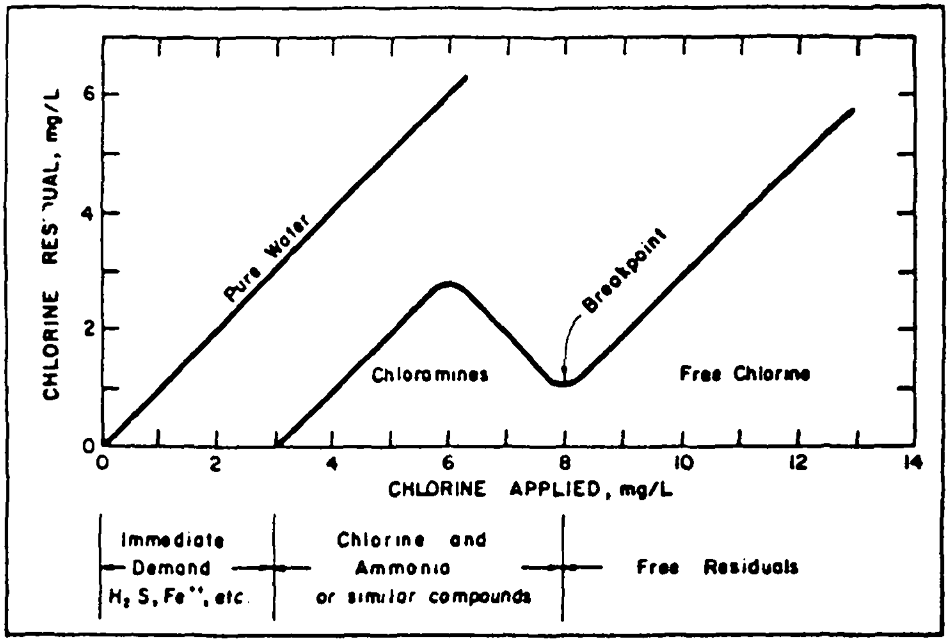

Figure 2. Graphical representation of the breakpoint chlorination reaction (U.S. EPA, 1983, p. III-10). The straight line at the left shows that chlorine residual is proportional to dosage in pure water. When impurities are present, they exert a chlorine demand.

When all of the ammonia and other chlorine-demanding organics have reacted with chlorine, the addition of more chlorine results in the hypochlorous acid oxidizing some of the same materials it just helped to create. The strange phenomenon observed is that the addition of more chlorine results in a decrease in the amount of residual (at this point a combined residual) indicated by the analytical procedure. When this oxidation is complete (called the breakpoint), then the addition of still more chlorine results in an increase in the amount of available chlorine measured. Note that the breakpoint must be surpassed before a free residual of chlorine can accumulate and persist.

It is important to be aware that the above illustration is considerably more complex than as described, because the reactions taking place are time-dependent. For this reason, a breakpoint curve is difficult to recreate and predict. Individual tests must be run, seasonally, and the data plotted to define the breakpoint for each water.

### iii. Factors Affecting Disinfection Efficiency of Chlorine

As indicated by the data of Table IIA, chlorine in the free state [HOCl + $(OCl)^-$] is quite an effective disinfectant. Rapid inactivation of most microorganisms can be obtained in a matter of minutes. However, effective disinfection with chlorine requires careful attention to:

1. Concentration of free available chlorine -- high enough in the plant so that it never drops below 0.2 mg/L at the farthest point in the distribution system (time basis),

2. Maintaining the pH as close to 7.0 as is practical or consistent with other water quality aspects, so as to maintain as much of the chlorine residual in the HOCl (hypochlorous acid) form,

3. Time of contact long enough to achieve the desired degree of microbial inactivation (i.e., to attain the CT value commensurate with the concentration of chlorine at the appropriate temperature).

4. Mixing. Baffle the chlorine contactor well to eliminate the possibility of short-circuiting of flow or provide an external mixing device.

Other factors also influence the chlorine disinfection process. Temperature has some effect on the ratio of HOCl to hypochlorite ion (see Figure 1) and has more effect on the disinfection rate (see Table IIA and Tables XI through XVI - taken from the June 25 draft of EPA's Proposed Surface Water Treatment Rule, U.S. EPA, 1987a), disinfection being faster at the higher temperatures. However, usually there is no means available to the operator to control temperature. Other tables are given in the Guidance Document (U.S. EPA, 1987e) relating residual chlorine levels to pH, concentration, and logs of Giardia inactivation.

### iv. Disinfection With Chlorine Gas

Chlorine is a toxic, yellow-green gas at ordinary temperatures and pressures. It is supplied in high strength steel cylinders, under sufficient pressure to liquefy the chlorine. When chlorine is required, simply opening the gas valve allows rapid vaporization of the liquid. As the liquid evaporates, its temperature falls. This could result in a slower rate of evaporation, and may require manifolding of containers or use of a vaporizer.

TABLE XI. CT VALUES FOR 99.9% INACTIVATION OF *Giardia* CYSTS BY FREE CHLORINE AT 0.5°C *

| Free Residual (mg/L) | pH |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
| ≤ 0.4 | 129 | 160 | 196 | 238 | 284 | 335 | 392 |
| 0.6 | 138 | 172 | 211 | 255 | 305 | 360 | 421 |
| 0.8 | 145 | 181 | 222 | 268 | 321 | 379 | 443 |
| 1.0 | 151 | 188 | 231 | 279 | 333 | 394 | 461 |
| 1.2 | 156 | 194 | 238 | 288 | 344 | 407 | 476 |
| 1.4 | 160 | 200 | 245 | 296 | 354 | 418 | 489 |
| 1.6 | 164 | 205 | 251 | 303 | 362 | 428 | 501 |
| 1.8 | 168 | 209 | 256 | 310 | 370 | 437 | 511 |
| 2.0 | 171 | 213 | 261 | 315 | 377 | 445 | 521 |
| 2.2 | 174 | 216 | 265 | 321 | 383 | 453 | 530 |
| 2.4 | 176 | 220 | 269 | 326 | 389 | 460 | 538 |
| 2.6 | 179 | 223 | 273 | 330 | 395 | 466 | 546 |
| 2.8 | 181 | 226 | 277 | 335 | 400 | 472 | 553 |
| 3.0 | 183 | 228 | 280 | 339 | 405 | 478 | 559 |

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

There are two basic types of gas chlorinators: *pressure operated, direct gas feed* and *vacuum operated, solution feed*. The former allows chlorine gas, under pressure, to be fed directly into the water to be disinfected. Solution feed units mix the gas with a side stream of water to form a solution of hypochlorous acid and hypochlorite ion, which then is mixed with the main stream.

### v. Disinfection With Sodium Hypochlorite Solution

Liquid chlorinators meter a previously prepared hypochlorite solution directly into the water to be disinfected. If the water supply system cannot afford the capital costs (see later subsection) and requirements associated with storing and handling chlorine gas, solutions of sodium hypochlorite can be purchased. It must be remembered that sodium hypochlorite solutions are more costly per pound of available chlorine and do not contain the concentrations of chlorine available in cylinders of chlorine gas. Also, hypochlorite solutions decompose if stored for prolonged periods. Thus, small systems using sodium hypochlorite should plan to store no more than a one-month supply.

TABLE XII. CT VALUES FOR 99.9% INACTIVATION OF *Giardia* CYSTS BY FREE CHLORINE AT 5°C *

| Free Residual (mg/L) | pH 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
|---|---|---|---|---|---|---|---|
| ≤ 0.4 | 92 | 114 | 140 | 169 | 202 | 239 | 280 |
| 0.6 | 98 | 123 | 150 | 182 | 217 | 257 | 300 |
| 0.8 | 104 | 129 | 158 | 191 | 229 | 270 | 316 |
| 1.0 | 108 | 134 | 165 | 199 | 238 | 281 | 329 |
| 1.2 | 111 | 139 | 170 | 206 | 245 | 290 | 339 |
| 1.4 | 114 | 142 | 175 | 211 | 252 | 298 | 349 |
| 1.6 | 117 | 146 | 179 | 216 | 258 | 305 | 357 |
| 1.8 | 119 | 149 | 183 | 221 | 264 | 311 | 365 |
| 2.0 | 122 | 152 | 186 | 225 | 269 | 317 | 371 |
| 2.2 | 124 | 154 | 189 | 229 | 273 | 323 | 378 |
| 2.4 | 126 | 157 | 192 | 232 | 277 | 328 | 383 |
| 2.6 | 127 | 159 | 195 | 235 | 281 | 332 | 389 |
| 2.8 | 129 | 161 | 197 | 239 | 285 | 337 | 394 |
| 3.0 | 131 | 163 | 200 | 242 | 288 | 341 | 399 |

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

In recent years, methods for on-site electrolytic generation of aqueous solutions of hypochlorite ion have been developed. In a two-cell unit, a brine solution (salt in water) is electrolyzed, producing a solution of hypochlorous acid in one cell and a solution of caustic (sodium hydroxide) in the other:

$$Na^+ + Cl^- + 2H_2O + e^- \text{ -----> }$$

sodium chloride  water  electron

$$HOCl + NaOH + H_2$$

hypochlorous acid  sodium hydroxide  hydrogen

TABLE XIII. CT VALUES FOR 99.9% INACTIVATION OF *Giardia* CYSTS BY FREE CHLORINE AT 10°C *

| Free Residual (mg/L) | pH 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
|---|---|---|---|---|---|---|---|
| ≤ 0.4 | 69 | 86 | 105 | 127 | 152 | 179 | 210 |
| 0.6 | 74 | 92 | 113 | 136 | 163 | 193 | 225 |
| 0.8 | 78 | 97 | 119 | 144 | 171 | 203 | 237 |
| 1.0 | 81 | 101 | 123 | 149 | 178 | 211 | 247 |
| 1.2 | 83 | 104 | 128 | 154 | 184 | 218 | 255 |
| 1.4 | 86 | 107 | 131 | 158 | 189 | 224 | 262 |
| 1.6 | 88 | 109 | 134 | 162 | 194 | 229 | 268 |
| 1.8 | 90 | 112 | 137 | 166 | 198 | 234 | 273 |
| 2.0 | 91 | 114 | 140 | 169 | 201 | 238 | 279 |
| 2.2 | 93 | 116 | 142 | 172 | 205 | 242 | 283 |
| 2.4 | 94 | 117 | 144 | 174 | 208 | 246 | 288 |
| 2.6 | 96 | 119 | 146 | 177 | 211 | 249 | 292 |
| 2.8 | 97 | 121 | 148 | 179 | 214 | 253 | 296 |
| 3.0 | 98 | 122 | 150 | 181 | 216 | 256 | 299 |

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

The advantages of this procedure are that purchasing and storing of gaseous chlorine and hypochlorite solutions are avoided. The primary technical disadvantages are the generation of hydrogen (which poses fire and explosion hazards), and the need to dispose of the caustic generated. In addition, the cost per pound, on a chlorine basis, typically is more than double for on-site electrolytic generation of hypochlorite ($0.30 to $0.35/lb) versus the cost of gaseous chlorine ($0.08 to $0.15/lb). However, site-specific considerations may make on-site hypochlorite generation the process of choice.

### vi. Disinfection With Solid Calcium Hypochlorite

Solid calcium hypochlorite is stable when properly packaged and sealed. Thus, a water supply system can purchase its annual requirements in a single procurement. Simply mixing the proper amount of solid with the appropriate volume of water to allow metering without clogging of pumps or metering valves is all that is required for use. Normally, an entire drum of calcium hypo-

TABLE XIV. CT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 15°C *

| Free Residual (mg/L) | pH |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
| ≤ 0.4 | 46 | 57 | 70 | 85 | 101 | 120 | 140 |
| 0.6 | 49 | 61 | 75 | 91 | 109 | 128 | 150 |
| 0.8 | 52 | 65 | 79 | 96 | 114 | 135 | 158 |
| 1.0 | 54 | 67 | 82 | 100 | 119 | 140 | 164 |
| 1.2 | 56 | 69 | 85 | 103 | 123 | 145 | 170 |
| 1.4 | 57 | 71 | 87 | 106 | 126 | 149 | 174 |
| 1.6 | 59 | 73 | 89 | 108 | 129 | 153 | 179 |
| 1.8 | 60 | 74 | 91 | 110 | 132 | 156 | 182 |
| 2.0 | 61 | 76 | 93 | 112 | 134 | 159 | 186 |
| 2.2 | 62 | 77 | 95 | 114 | 137 | 161 | 189 |
| 2.4 | 63 | 78 | 96 | 116 | 139 | 164 | 192 |
| 2.6 | 64 | 79 | 97 | 118 | 141 | 166 | 194 |
| 2.8 | 65 | 80 | 99 | 119 | 142 | 168 | 197 |
| 3.0 | 65 | 81 | 100 | 121 | 144 | 170 | 199 |

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

chlorite is made into solution. This avoids the partial use of a container, with attendant uncertainties of proper resealing and loss of strength.

### vii. Chlorination System Design

Choice of the form of chlorination system to be used, whether gaseous chlorine, dry calcium hypochlorite, sodium hypochlorite solution or on-site generation, depends upon a number of factors which include the following:

- availability of chlorine source chemical,
- capital cost of the facility,
- operation and maintenance costs for the equipment,
- chemical costs,
- location of the facility,
- operator skills available,
- safety.

TABLE XV. CT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 20°C *

| Free Residual (mg/L) | pH | | | | | | |
|---|---|---|---|---|---|---|---|
| | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
| ≤ 0.4 | 34 | 43 | 53 | 64 | 76 | 90 | 105 |
| 0.6 | 37 | 46 | 56 | 68 | 82 | 96 | 113 |
| 0.8 | 39 | 48 | 59 | 72 | 86 | 101 | 119 |
| 1.0 | 40 | 50 | 62 | 75 | 89 | 105 | 123 |
| 1.2 | 42 | 52 | 64 | 77 | 92 | 109 | 127 |
| 1.4 | 43 | 53 | 66 | 79 | 95 | 112 | 131 |
| 1.6 | 44 | 55 | 67 | 81 | 97 | 114 | 134 |
| 1.8 | 45 | 56 | 68 | 83 | 99 | 117 | 137 |
| 2.0 | 46 | 57 | 70 | 84 | 101 | 119 | 139 |
| 2.2 | 46 | 58 | 71 | 86 | 102 | 121 | 142 |
| 2.4 | 47 | 59 | 72 | 87 | 104 | 123 | 144 |
| 2.6 | 48 | 60 | 73 | 88 | 106 | 125 | 146 |
| 2.8 | 48 | 60 | 74 | 90 | 107 | 126 | 148 |
| 3.0 | 49 | 61 | 75 | 91 | 108 | 128 | 150 |

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

Each of the methods of chlorination will provide the same disinfecting power on a pound for pound basis of available chlorine when utilized at the same pH. However, each of the systems must be approached differently in terms of basic design and safety.

Sufficient chlorine must be provided to satisfy the chlorine demand of the water at the point of chlorine addition, plus an additional amount to maintain the required residual after a specified contact time (see CT values in Tables XI to XVI). The relative dosages of the various chemical sources of hypochlorite ion [(OCl)$^-$] in solution can be determined; these frequently will depend upon the point of chlorine application in the process.

The chlorine demand of raw water usually is far higher than that of finished water. In any case, a minimum contact time, commensurate with the CT value, the pH of the water, and the temperature, must be maintained to assure the appropriate inactivation of Giardia lamblia and viruses. If chlorine also is used for secondary disinfection, a residual of not less than 0.2 mg/L must be provided at all points throughout the distribution system.

TABLE XVI. CT VALUES FOR 99.9% INACTIVATION OF *Giardia* CYSTS BY FREE CHLORINE AT 25°C *

| Free Residual (mg/L) | pH | | | | | | |
|---|---|---|---|---|---|---|---|
| | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 |
| ≤ 0.4 | 23 | 29 | 35 | 42 | 51 | 60 | 70 |
| 0.6 | 25 | 31 | 38 | 46 | 54 | 64 | 75 |
| 0.8 | 26 | 32 | 40 | 48 | 57 | 68 | 79 |
| 1.0 | 27 | 34 | 41 | 50 | 59 | 70 | 82 |
| 1.2 | 28 | 35 | 43 | 51 | 61 | 73 | 85 |
| 1.4 | 29 | 36 | 44 | 53 | 63 | 75 | 87 |
| 1.6 | 29 | 36 | 45 | 54 | 65 | 76 | 89 |
| 1.8 | 30 | 37 | 46 | 55 | 66 | 78 | 91 |
| 2.0 | 30 | 38 | 47 | 56 | 67 | 79 | 93 |
| 2.2 | 31 | 39 | 47 | 57 | 68 | 81 | 94 |
| 2.4 | 31 | 39 | 48 | 58 | 69 | 82 | 96 |
| 2.6 | 32 | 40 | 49 | 59 | 70 | 83 | 97 |
| 2.8 | 32 | 40 | 49 | 60 | 71 | 84 | 99 |
| 3.0 | 33 | 41 | 50 | 60 | 72 | 85 | 100 |

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

### Chlorination With Gaseous Chlorine:

Chlorine is supplied in high strength steel cylinders with minimum chlorine capacities of 100 and 150 pounds, up to one ton, and in tank cars under sufficient pressure to liquefy the chlorine. Major manufacturers of gaseous chlorine are listed in Table XVII. However, the quantity consumed by small water systems normally would be purchased from local suppliers which are listed in the local telephone directory yellow pages under "Chemical Suppliers" or "Swimming Pool Suppliers".

Direct feed chlorinators add gas under pressure directly into the water to be disinfected. This type of unit normally is used only when electrical power is unavailable nor sufficient water pressure differential to operate a solution feed unit. This is a site-specific application which will not be discussed further.

TABLE XVII. MANUFACTURERS OR PACKAGERS OF GASEOUS CHLORINE

| Name | Address |
|---|---|
| Ashland Chemical Company<br>Petrochemical Division | P.O. Box 2219, Columbus, OH 43216 |
| Dow Chemical U.S.A. | 2020 Dow Center, Midland, MI 48640 |
| FMC Corp.,<br>Industrial Chemical Group | 2000 Market Street, Philadelphia, PA 19103 |
| Georgia-Pacific | P.O. Box 105605, Atlanta, GA 30348 |
| Kaiser Aluminum & Chemical Corp.<br>Industrial Chemical Division | 300 Lakeside Drive, Oakland, CA 94643 |
| Kaiser Chemicals | 30100 Chagrin Boulevard, Cleveland, OH 44124 |
| Kuehne Chemical Co., Inc. | 86 Hackensack Avenue, Kearny, NJ 07032 |
| Occidental Chemical Corp.<br>Industrial & Specialty Chemicals | 360 Rainbow Blvd. South, P.O. Box 728, Niagara Falls, NY 14302 |
| Olin Corporation | 120 Long Ridge Road, Stamford, CT 06904 |
| Pennwalt Corporation<br>Inorganic Chemicals Division | 3 Parkway, Philadelphia, PA 19102 |
| Stauffer Chemical Co. | Westport, CT 06881 |
| Vulcan Materials Co.,<br>Chemicals Division | P.O. Box 7689, Birmingham, AL 35253 |

Solution feed units mix chlorine gas with a side stream of water to form a hypochlorous acid solution, which then is injected into the main stream. Solution feed chlorinators operate on a vacuum controlled basis, automatically shutting off if the side stream flow is interrupted. This type of unit, shown in Figure 3, is preferable for safety reasons over direct feed units.

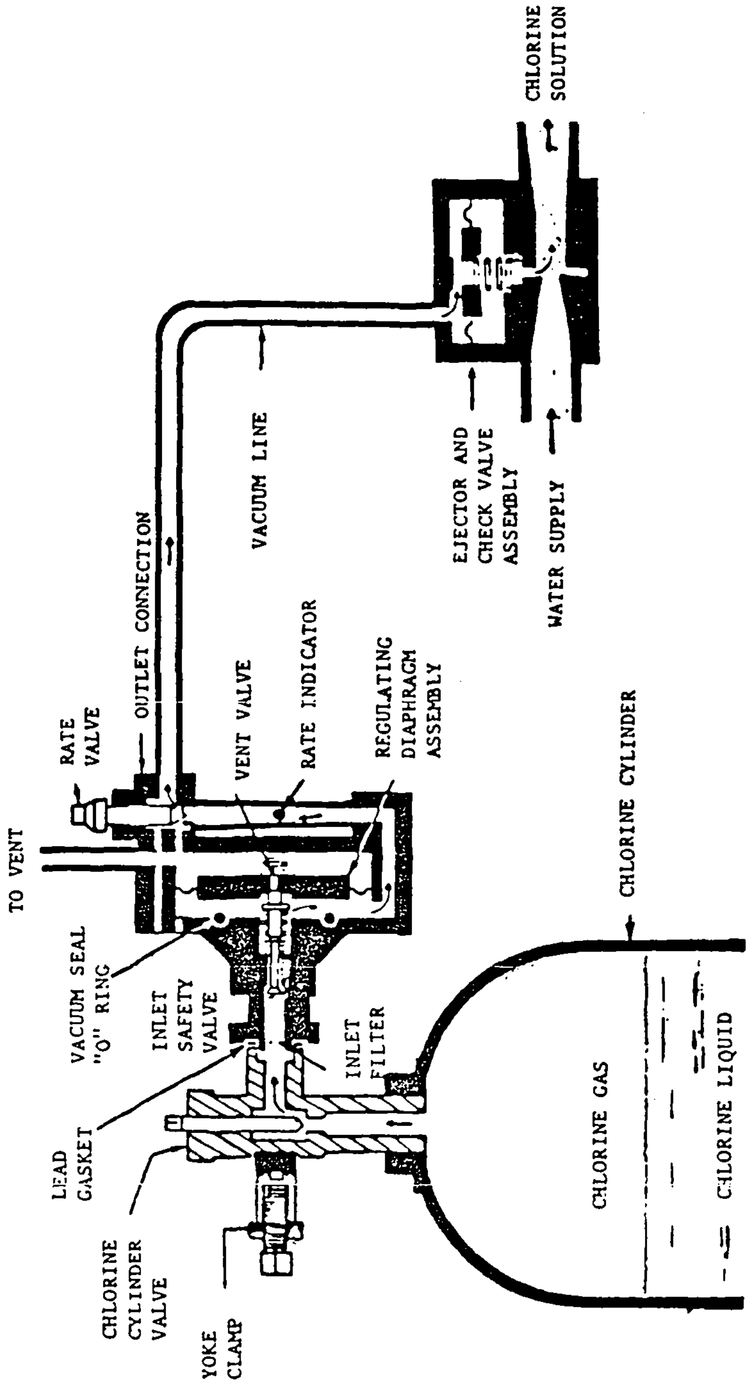

Figure 3. Solution feed gas chlorination system. (Courtesy of Capital Controls Co., Inc.)

The basic solution feed gas chlorinator includes the following components:

- gas shut-off valve to interrupt gas flow;
- vacuum regulator, or
- gas flow indicator;
- adjustable gas flow controller;
- check valve;
- venturi type gas injector.

The market for supply of gas chlorinators is quite competitive, as illustrated by Table XVIII, which provides a partial listing of suppliers of these types of units.

Well established standards for design of gas chlorination systems exist in standard waterworks industry literature (Great Lakes-Upper Mississippi River Board of State Sanitary Engineers, 1985; Am. Water Works Assoc., 1985). The following points are provided to highlight possible design questions:

- Under normal conditions, the withdrawal rate of chlorine gas from a single 150-lb liquid chlorine container is more than adequate to satisfy the chlorine demand of the water processed for 5,000 persons (5,000 persons x 100 gal/capita/day = 500,000 gal/day), as illustrated by the following calculation:

  $$40 \text{ lbs/day}/8.34 \text{ lbs/gal} \times 0.5 \text{ mgd} = 9.6 \text{ mg/L}$$

  Weighing scales to provide a positive measure of chlorine usage should be provided. A device for automatic switchover from empty cylinder to full cylinder reduces manpower requirements, and increases chlorination reliability.

- Chlorine cylinders are heavy and bulky, even when empty. Provision should be made for easy removal of gas cylinders from the delivery truck and their movement to the chlorine storage room. A special cart should be assigned to the chlorination facility for cylinder transport. Stairways, narrow doorways, and passages should not be part of the route from delivery to storage. Any cylinders stored upright should be fastened securely to the walls to prevent their falling, which can shear the neck and cause a rapid discharge of the gas - resulting in two hazards - exposure to high concentrations of chlorine, and the danger of physical injury from the cylinder, which can become a fast-moving projectile.

- Chlorinators should be located as close as possible to the point of chlorine application. Provision should be made for regular inspection of chlorine gas and solution lines.

TABLE XVIII. SOME GAS CHLORINATOR MANUFACTURERS

| Name | Address |
|---|---|
| Capital Controls Co., Inc. | Box 211, Colmar, PA 18915 |
| Chlorinators Inc. | 733 NE Dixie Highway, Jensen Beach, FL 33457 |
| Fischer & Porter Co. | County Line Rd., Warminster, PA 18974 |
| Hydro Instruments Inc. | 492 Richlandtown Pike, Box 615, Quakertown, PA 18951 |
| Modern Process Systems Inc. | 14834 Highland Road, Baton Rouge, LA 70810 |
| Wallace & Tiernan, Division of Pennwalt Corp. | 25 Main Street, Belleville, NJ 07109 |

- The 150-lb cylinders should be operated so that the chlorine is used at a rate no greater than one pound per day per degree Fahrenheit per cylinder. If chlorine is removed at a greater rate, evaporation of the liquid chlorine will cool the chlorine and reduce the pressure and gas feed. Multiple cylinders should be used for higher daily flow rates. Frost formation on the cylinder and vacuum lines is an indication of excessive cooling and requires system review.

## Chlorination With Sodium Hypochlorite

Sodium hypochlorite, usually supplied in concentrations of 5 and 15% available chlorine, is available commercially only in the solution form. In this form, it is easier to handle than gaseous chlorine or calcium hypochlorite. However, sodium hypochlorite solutions will lose their disinfecting (oxidizing) power during storage, and should be stored in a cool, dark, dry area.

The material is supplied in glass or plastic bottles, carboys, or in lined drums ranging in size from 0.5 to 55 gal. Bulk shipment by tank truck also is a common form of transport. No more than a one-month supply of the chemical should be purchased to prevent loss of available chlorine.

### Chlorination With Calcium Hypochlorite

This material is supplied as a white solid which is quite corrosive, and gives off a strong chlorinous odor. It contains approximately 65% available chlorine, is readily soluble in water, and is available in granular, powdered, or tablet form. It is provided in 2, 5, 8, and 35 lb cans and in 100, 300, and 800 lb drums. The containers generally are resealable.

Calcium hypochlorite is hygroscopic (readily absorbs moisture), and reacts slowly with atmospheric moisture to form chlorine gas. Therefore, shipping containers must be emptied completely or carefully resealed. It is not feasible to handle this material in bulk handling systems.

The contents of a calcium hypochlorite container are emptied into a mixing tank where it is readily and completely dissolved in water. The resulting quite corrosive solution is stored in and fed from a stock solution vessel constructed of corrosion-resistant materials such as plastic, ceramic, glass, or rubber-lined steel. Dosage of the solution at 1% or 2% available chlorine content is by diaphragm type, chemical feed/metering pump.

### viii. **Chlorination Systems Costs** (U.S. EPA, 1983)

In the following discussion, cost data are presented for the three types of chlorination systems discussed above, and as related to their use at small water treatment systems, sized to treat water volumes up to at least 1 mgd. The larger systems will have to change chlorine cylinders more frequently than will the smaller systems. For example, a 1 mgd water treatment plant using an average chlorine dosage of 5 mg/L will use nearly 42 lbs of chlorine per day. Thus, a 150-lb cylinder of chlorine will last between three and four days at this size plant.

Operating and maintenance costs presented do not include chemical costs. These will vary depending upon the volume of water treated and the dosage required.

Cost data were obtained primarily from two sources (Hansen et al., 1979; U.S. EPA, 1983). However, a more recent publication by Gumerman et al. (1986) contains additional cost data developed specifically for small water systems. Unfortunately, this latest publication became available after the present document had been assembled.

## Solution-Feed Chlorination With Gaseous Chlorine

### Equipment Costs

Table XIX shows a detailed cost breakdown obtained during May 1980 from three vendors of chlorination equipment. Data are presented in terms of a basic gas chlorination system, as well as costs for five increasingly complex systems. The basic system includes equipment to handle two 150-lb chlorine cylinders, two cylinder-mounted chlorine gas regulators, automatic changeover valve, and chlorine gas flow and rate valve ejector (with system backup). Alternate #1 adds two scales, a gas mask, and a diffuser corporation cock (to allow connection under water line pressure). Alternate #2 adds a flow-pacing chlorine addition system. Alternate #3 adds a flow meter. Alternate #4 adds a booster pump and piping. Alternate #5 adds a chlorine leak detector.

The cost comparisons in Table XIX present a basic-to-most-sophisticated comparison between the various system configurations in which gaseous chlorination systems can be purchased. Costs are comprised of equipment, installation, safety enclosure, contractor's overhead and profit, plus 10% engineering fee for the basic system estimates.

The basic (lowest cost) gaseous chlorination system costs about $9,350; with all options added, the most sophisticated gaseous chlorination system costs $16,050, in May 1980 dollars.

### Operation and Maintenance Costs

Hansen et al. (1979) state that in general, operation and maintenance costs for chlorination systems treating 2,500 gpd to 1 mgd are independent of flow. Process energy requirements are for the booster pump only, and are about 1,630 kWh/yr. Building energy requirements for a 25 $ft^2$ building to house the system would be 2,560 kWh/yr. Maintenance material requirements would be only for miscellaneous repair of valving, electrical switches, and other equipment, and would total about $40/yr. Labor requirements are for periodic checking of equipment, with an average requirement of 0.5 h/day, or 183 h/yr.

O&M costs of $2,457/yr are summarized in Table XX. Note that power costs were taken at $0.07/kWh and labor at $10.00/h. These were prevalent rates in 1982 and were used (U.S. EPA, 1983) to update the corresponding energy and labor costs made earlier by Hansen et al. (1979).

TABLE XIX. CAPITAL COSTS FOR GAS CHLORINATION (1980 Dollars*)

| | | |
|---|---|---|
| EQUIPMENT COSTS FOR A SYSTEM OF 100 lbs/day (2 kg/h) OR LESS | | |
| Basic System** | Average | $1,873 |
| | High | 2,300 |
| | Low | 1,320 |
| Alternate #1 - add scales, mask diffuser, corporation cock | Average | 770 |
| Alternate #2 - add flow pacing - existing signal | Average | 1,694 |
| Alternate #3 - add flow meter & signal, 8 in. or less | Average | 2,068 |
| Alternate #4 - add booster pump & piping | Average | 792 |
| Alternate #5 - add $Cl_2$ gas detector | Average | 1,382 |
| INSTALLATION | Average | 1,167 |
| | High | 1,500 |
| | Low | 1,000 |
| SAFETY ENCLOSURE | Average | 3,500 |
| | High | 6,000 |
| | Low | 2,000 |
| CONTRACTOR'S OVERHEAD AND PROFIT (20%) | | 1,869 |
| ENGINEERING FEES (10%) | | 934 |
| TOTAL CAPITAL COST | | |
| Basic System | | $9,343 |
| Most Sophisticated (with Alternate #5) | | $16,049 |

* May 1980 quotes (three vendors)

** Basic system includes two 150-lb chlorine cylinders, two cylinder-mounted regulators, automatic changeover valve, chlorine gas flow rate valve, and ejector (system with backup)

TABLE XX. O&M SUMMARY FOR SOLUTION-FEED GAS CHLORINATION

| Item | Requirements* | | Costs |
|---|---|---|---|
| ELECTRICAL ENERGY: | | | |
| Process | 1,630 kWh/yr x $0.07 | = | $ 114.10 |
| Building | 2,560 kWh/yr x $0.07 | = | 179.20 |
| Total | 4,190 kWh/yr x $0.07 | = | $ 293.30 |
| MAINTENANCE MATERIAL: | | = | $ 40/yr |
| LABOR: | 183 h/yr x $10/h | = | $1,830 |
| TOTAL ANNUAL O&M COST | | | $2,457 |

* Estimates of energy, maintenance, and labor made by Hansen et al. (1979).

### Chemical Costs

In 150-lb cylinders, chlorine cost $0.47/lb in the Washington, DC/Baltimore area in January 1983. In 1987, the cost for gaseous chlorine in 150-lb cylinders is $0.37/lb, when purchased in ton quantities. For purposes of this discussion applicable to small water systems, the $0.47/lb will be considered as current.

Assuming a chlorine dosage of 5 mg/L, gaseous chlorine chemical costs would be about $18/yr to treat 2,500 gpd, and about $7,150/yr to treat 1 mgd.

To calculate costs for gaseous chlorine at lower or higher dosages, the following formula can be used:

$$\frac{\text{dosage (mg/L)} \times \text{no. of L dosed/day} \times Cl_2 \text{ cost/lb}}{1000\ \text{(mg/g)} \times 454\ \text{g/lb)}} = Cl_2 \text{ cost/day}$$

## Sodium Hypochlorite Solution Feed

### Equipment Costs

Table XXI displays estimates obtained during May 1980 from two vendors of sodium hypochlorite chlorination equipment. Data are presented for the basic liquid hypochlorination system which includes two metering pumps (one serves as standby), solution tank, diffuser, and appropriate quantities of tubing. However,

TABLE XXI CAPITAL COSTS -- LIQUID CHLORINATORS*

| EQUIPMENT COST<br>(basic system**) | | Electrically<br>Activated | Hydraulically<br>Activated |
|---|---|---|---|
| | Avg. | $ 1,800 | $ 2,266 |
| | High | 2,300 | 2,782 |
| | Low | 1,300 | 1,750 |
| INSTALLATION | | 500 | 1,000 |
| SITE WORK | | 250 | 250 |
| CONTRACTOR'S OVERHEAD & PROFIT (20%) | | 729 | 1,004 |
| ENGINEERING FEES (10%) | | 364 | 503 |
| Alternate #1: add diffuser corporation cock & anti-siphon backflow preventer | | 165 | 231 |
| Alternate #2: add safety enclosure (housing) | | 6,930 | 6,930 |
| Alternate #3: add flow pacing existing signal | | --- | 1,485 |
| Alternate #4: add flow meter signal, 8 in. or less | | --- | 1,452 |
| TOTAL CAPITAL COST: | | | |
| Basic System (Equipment + Installation + Site Work + Overhead & Profit + Engineering Fees | | $3,643 | $5,023 |
| Most Sophisticated (with Alternate #2) | | $10,738 | --- |
| (with Alternate #4) | | --- | $15,121 |

* May 1980 quotes (two vendors)

** Basic System includes two metering pumps (one standby), tubing, solution tank, and diffuser two types of basic system are costed, one activated electrically, the other activated hydraulically. The basic systems can be supplemented, and costs of four increasingly sophisticated alternatives also are presented in this table. Alternate #1 adds a diffuser corporation cock and anti-siphon backflow preventer. Alternate #2 adds a safety housing enclosure. Alternate #3 adds a flow-pacing system, and Alternate #4 adds a flow meter and signal.

The total capital costs for the basic and most sophisticated systems are:

| | basic system | most sophisticated system |
|---|---|---|
| Electrically Activated | $3,643 | $10,738 |
| Hydraulically Activated | $5,023 | $15,121 |

## Operating and Maintenance Costs

As with solution-feed gas chlorinators, O&M requirements are independent of flow for plants treating 2,500 gpd to 1 mgd (Hansen et al., 1979). Process energy requirements are for the diaphragm metering pump and amount to 570 kWh/yr. Building energy requirements for a 25 $ft^2$ building would be 2,560 kWh/yr. Maintenance materials would be required only for minor component repair -- costs which are estimated at $20/yr.

Labor is required for periodic mixing of the sodium hypochlorite solution, as well as for checking of the equipment. Based on a requirement of 1 h/day, the annual labor requirement would be 365 h/yr.

Annual O&M costs of $4,108 are summarized in Table XXII. Note again that power costs are based on $0.07/kWh and labor costs of $10.00/h.

## Chemical Costs

Sodium hypochlorite customarily is sold as a 15% (by weight) solution. In July 1987, the cost of a 15% solution in 1,500 gal tanks in the Washington, DC/Baltimore area was $0.50/gal. A small water utility treating 2,500 gal/day with 5 mg/L of chlorine as sodium hypochlorite solution would require about 64 gal/yr. At $0.50/gal, this utility would spend about $32/yr. A 1 mgd facility using 5 mg/L of chlorine would require 400 times more hypochlorite solution, and would spend $12,800/yr.

TABLE XXII O&M COST SUMMARY FOR SODIUM HYPOCHLORITE SOLUTION FEED (U.S. EPA, 1983)

| Item | Requirements* | | | | Cost |
|---|---|---|---|---|---|
| ELECTRICAL ENERGY | | | | | |
| Process | 570 kWh/yr | x | $0.07 | = | $ 39.90 |
| Building | 2,560 kWh/yr | x | $0.07 | = | $ 179.20 |
| Subtotal | 3,130 kWh/yr | x | $0.07 | = | $ 219.10 |
| MAINTENANCE MATERIAL | | | | | $ 20/yr |
| LABOR | 365 h/yr | x | $10/h | = | $3,650 |
| <u>Total Annual O&M Cost</u> | | | | | <u>$4,108</u> |

* amounts estimated by Hansen et al. (1979)

However, it should be realized that the cost for sodium hypochlorite solution is about three times the cost of gaseous chlorine in equivalent quantities, and that 0.9 lb of 15% NaOCl solution is equivalent in oxidation potential to one pound of gaseous chlorine. These ratios between the two forms of chlorine will assist in cost calculations.

## Calcium Hypochlorite Solution Feed

Equipment costs and operating and maintenance costs for this method of disinfection should be very close to those for sodium hypochlorite feed systems. Solutions of calcium hypochlorite are prepared in a mixing tank, then transferred to a day tank (a tank which holds enough solution to last for one day), then injected into the water stream using a diaphragm metering pump.

### Chemical Costs

Solid calcium hypochlorite, $Ca(OCl)_2$, contains 65% available chlorine. Therefore, one pound contains 65 lb of available chlorine. Since a 2,500 gal/day treatment plant requires 0.104 lb of chlorine per day (at an average dosage of 5 mg/L), 0.104/-0.65 = 0.16 lb of $Ca(OCl)_2$ per day is required with which to prepare a solution for metering into the water to be treated.

During July 1987, calcium hypochlorite was selling for \$0.95/lb in the Washington, DC/Baltimore area. Over a one year period, the 2,500 gal/day facility will require 0.16 lb x 365 days = 58.4 lbs of $Ca(OCl)_2$, x \$0.95/lb = \$55.48/yr. A 1 mgd facility, which uses 400 times the amount of chlorine, therefore will spend \$22,192/yr for $Ca(OCl)_2$.

## b. Ozone

### i. Characteristics and Properties of Ozone

Ozone ($O_3$) is a very powerful oxidizing agent, second only to elemental fluorine among readily available chemicals. Because of its strong oxidizing ability, ozone also is a powerful disinfectant. It is an unstable gas at ambient temperatures and pressures, and decomposes rapidly to oxygen (from which it is made) at temperatures above 35°C. For this reason, it cannot be manufactured and packaged at a central manufacturing plant, as can chlorine. Therefore, ozone must be generated on-site and used at once.

Ozone has a characteristic odor which can be detected by most humans at low concentrations (0.01 to 0.05 ppm by volume), far below the levels of acute toxicity. However, olfactory fatigue has been noted in some instances. This means that as the length of exposure to an ozone-containing atmosphere increases, the odor of ozone may become less noticeable.

When added to water, ozone dissolves only partially. That is to say that ozone is only slightly soluble in water, about 13-20 times the solubility of oxygen. The solubility of ozone in water is governed by Henry's Law, which states that the mass of ozone that will dissolve in a given volume of water, at constant temperature, is directly proportional to the partial pressure of the ozone gas above the water. Consequently, proper design of the ozone contacting system is very important to the proper application of ozone to water (see later discussion - iii).

The stability of ozone is greater in air than in water, but is not excessively long in either case. The half-life of ozone in water has been reported to range from 8 minutes to 14 hours, depending on the phosphate and carbonate concentrations of the water (Grunwell et al., 1983). With no phosphates or carbonates and the water adjusted to pH 7.0 with sodium hydroxide, the half-life was 8 minutes.

## ii. Generation of Ozone

For the on-site generation of ozone by means of corona discharge (the procedure used most for water treatment), an oxygen-containing gas (air, oxygen-enriched air, or pure oxygen) is dried and cooled, then passed between two electrodes separated by a discharge gap and a dielectric material across which high voltage potentials are passed. In recent years, the more modern ozone generating equipment has been designed to operate at high frequencies rather than high voltages.

Figure 4 is a schematic diagram of the essential components of a corona discharge ozone generator. For small water plants, ambient air dried to a dew point of minus 65°C (-65°C) will be the source gas fed to the ozone generator. It is imperative that the ambient air be dried rigorously in order to maximize the yield of ozone produced, as well as to minimize the formation of corrosive nitrogen oxides.

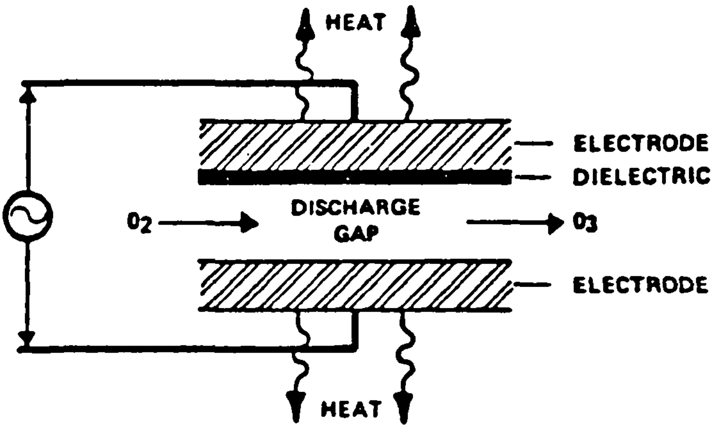

Figure 4. Typical corona discharge cell ozone generating configuration.

With properly dried air, the output from a corona discharge ozone generator will be dried, cooled air, containing 1% to 3.5% of ozone, which is partially soluble in water (about 13-20 times the solubility of oxygen). This produced mixture of ozone in air then must be mixed with the water to be treated, by a process known as contacting (see later discussion - iii).

Ozone also can be generated by passing UV radiation through ambient air. However, in this procedure, only small quantities of ozone can be generated, and at much lower concentrations (0.1 to 0.001%) than can be generated by corona discharge. This concentration is considered insufficient to provide enough ozone in water to cause a significant amount of oxidative or disinfective treatment.

When oxygen is used as the feed gas to the ozone generator, the concentration of ozone produced is effectively doubled over that produced when properly dried air is employed. This means that oxygen containing 2% to 7% (by weight) of ozone is generated in the same size corona discharge ozone generator and for the same expenditure of electrical energy as when dried air is used.

In the United States today, there are at least 34 operational water treatment plants using ozone. Only the new 540 mgd plant in Los Angeles is using oxygen as the feed gas. In the rest of the world, where ozone is used more extensively than currently in the U.S., only half a dozen water treatment plants are known to be using oxygen as the feed gas.

When the properly dried air or oxygen passes through the ozone generator, part of the oxygen dissociates as a result of being exposed to the high energy electrical field of the corona discharge:

$$\underset{\text{oxygen}}{O_2} + e^- \text{------>} 2[O] \text{ "fragments"}$$

These oxygen "fragments" are highly reactive, and they combine rapidly with molecular oxygen, forming the triatomic molecule, ozone:

$$\underset{\text{oxygen fragments}}{2[O]} + \underset{\text{oxygen}}{2\,O_2} \text{------>} \underset{\text{ozone}}{2\,O_3}$$

The overall reaction to produce ozone is the sum of the above reactions:

$$\underset{\text{oxygen}}{3\,O_2} + \underset{\text{energy}}{e^-} \text{<----->} \underset{\text{ozone}}{2\,O_3}$$

The reaction to produce ozone is reversible, meaning that once formed, ozone decomposes back to oxygen. This reverse reaction occurs quite rapidly above 35°C. Therefore, because reactions involving high energy electrical discharges also are accompanied by generation of considerable heat, ozone generators are designed to include a high degree of cooling, in order to minimize ozone losses by decomposition.

### iii. Contacting of Ozone With Water

Because ozone is only partially soluble in water (13-20 times that of oxygen), the manner with which it is contacted with the water to be treated is of primary importance. In turn, the manner of contacting ozone with water depends upon the particular ozonation job or jobs to be accomplished.

For purposes of illustration, there are basically two types of reactions involving ozone: fast and slow. Fast ozonation reactions include the inactivation of microorganisms (disinfection), oxidations of iron, manganese, sulfide ions, nitrite ions, some organics, and lowering turbidity levels. On the other hand, other ozone oxidations, such as oxidation of many organic materials (specifically many pesticides and VOCs), are kinetically rather slow.

As a result, for the fast ozone reactions, the contacting objective is to add the requisite amount of ozone to the water as rapidly as possible, so that the solute being oxidized or inactivated will react as rapidly as possible. The rate of this type of ozonation reaction is dependent on the rate of transfer of ozone into solution. This type of reaction is termed "mass transfer controlled", and contact times, therefore, are relatively short.

For example, for disinfection with ozone, ozone is added first to satisfy the ozone demand of the water and to create a residual dissolved ozone level, then to maintain the requisite residual of ozone for a given period of time.

Slower ozone oxidations are dependent upon maintaining a low residual concentration of ozone in the water, but over a much longer length of time, because the chemical reaction rates are slow. These types of reactions are termed "reaction rate controlled".

Ozone can be generated under positive or negative air pressure. If generated under positive pressure, the ozone-containing air exits the ozone generator at approximately 15 psig. This is sufficient pressure for the gas to pass through porous diffusers installed at the base of a 16 foot column or tank of water. Fine bubbles containing ozone and air (or oxygen) rise slowly through this water column. During the time of bubble rise, the ozone contained in the bubbles diffuses from the gas phase into the water phase, where oxidation and/or disinfection takes place.
The 16 ft height of water column maximizes the amount of ozone mass transferred from the tiny bubbles as they rise.

Other types of positive pressure ozone contactors include packed columns, static mixers, and high speed agitators. The water to be treated also can be sprayed through small orifices into an ozone-containing atmosphere.

When ozone is generated under negative pressure, the air or oxygen is drawn through the feed gas preparation system, then through the ozone generator and into the contactor. The sub-atmospheric pressure can be created by employing a submerged turbine as the contactor. Thus, when the turbine is turned on, its whirling action creates a slight vacuum, drawing air through the entire ozonation system.

Other methods of creating sub-atmospheric pressure which are in common practice are by use of injectors or Venturi-type nozzles. Water to be treated is pumped past a small orifice (injector) or through a Venturi nozzle. In either case, a slight vacuum is created, which can be used to draw the air/oxygen through the ozonation system. Contacting takes place during the mixing of the gas with the flowing water.

It can be appreciated that the diffuser and packed tower contactors require no energy to operate, whereas high speed agitators, static mixers, and all of the negative pressure contactors require energy for their operation.

As excellent discussion of the various types of ozone contactors has been assembled by Masschelein (1982).

### iv. Destruction of Contactor Exhaust Gas

No matter how well designed the ozone contactor, it is rare, if ever, that 100% transfer of ozone to the water occurs. Therefore, there will always be some excess ozone in the gases which exit the ozone contacting system. Particularly for disinfection with ozone, during which a dissolved residual of ozone is present for a predetermined length of time, there will always be ozone present in the contactor exhaust gases (off-gases). This excess ozone either must be reused or destroyed before discharge of the gases to the plant atmosphere.

Reuse of ozone can be effected if two stages of ozonation (one for oxidation, one for disinfection) are designed into the water treatment process. In this event, contactor exhaust gases from the primary ozonation step are drawn into the second ozonation stage, for example, by means of a submerged turbine.
Even well-designed reuse of ozone in a second stage still will leave some excess ozone in the final exhaust gases, and this must be destroyed before discharge. Destruction of ozone (to produce oxygen from which it is generated) is accomplished by several methods:

- thermal destruction -- at 300-350°C, ozone decomposition requires only a few seconds,
- catalytic destruction -- at ambient temperatures with the appropriate catalyst (metal or metal oxide),
- adsorption and decomposition on moist granular activated carbon,
- exposure to UV radiation (254 nm wavelength).

This latter method is in use only in very large treatment plants, because even at 254 nm wavelength, there is a small amount of ozone generated.

### v. Chemistry of Ozone in Water

Unlike chlorine, ozone does not react with water to produce disinfecting species. However, above pH about 6, ozone does decompose in water to produce the more reactive hydroxyl free radical:

$$O_3 + H_2O \text{ -----> } O_2 + 2(OH)^{\cdot}$$

This reaction is accelerated at the higher pH values (above 8). In addition, hydroxyl free radicals are produced whenever ozone is exposed to UV radiation, or when ozone is in the presence of hydrogen peroxide. Ozone oxidation rates of some refractory organic materials are greatly accelerated by the simultaneous addition of UV radiation or $H_2O_2$ because of the formation of hydroxyl free radicals.

Thus, when ozone is added to water it can react as the $O_3$ molecule, as the hydroxyl free radical, or as a mixture of both.

Bicarbonate and carbonate ions are good scavengers of free radicals; therefore waters containing high alkalinity levels will quickly destroy the hydroxyl free radicals produced by the decomposition of ozone, and eliminate the benefits of the free radical oxidative mechanisms.

### vi. Establishing An Ozone Residual

In order to attain the appropriate CT value to achieve 99.9% inactivation of Giardia lamblia cysts (Table IIA) a measurable residual level of ozone must be developed in water and maintained for the appropriate period of time. In operating drinking water treatment plants using ozone for disinfection (primarily in France, but also in many other countries of the world), it is customary to attain a dissolved ozone residual concentration of approximately 0.4 mg/L, then to maintain this concentration for a period of time.

It can be appreciated that the water entering the ozone-for-disinfection contacting chamber has the highest ozone demand, whereas water exiting the contacting chamber has the lowest ozone demand. Therefore, part of the function of the ozone contacting system is to satisfy the ozone demand of the water. Since disinfection is a mass transfer type of reaction (fast), a certain percentage of ozone is utilized initially to satisfy the ozone demand. After the ozone demand is satisfied, the contacting task becomes one of maintaining a specific ozone concentration for a specific time period.

These two tasks normally are conducted in two different contacting chambers, with the larger amount of ozone being applied to the first chamber. This procedure, which is employed to minimize the amount of ozone added, is shown in Figure 5. Approximately two-thirds of the total ozone required is added to the first chamber, in which the ozone demand of the water is satisfied, and a residual ozone level of about 0.4 mg/L is attained. The balance of the ozone (one-third) is added to the second chamber, in which the 0.4 mg/L ozone residual is maintained.

To attain the necessary contact time for the ozone with a 0.4 mg/L ozone residual, it is simply a matter of dividing 0.4 into the CT value from Table IIA taken at the appropriate temperature. The product is the minimum contact time (in minutes) required. Table XXIII shows the CT values and contact times required for an ozone residual of 0.4 mg/L at various temperatures.

TABLE XXIII. CT VALUES AND CONTACT TIMES FOR OZONE TO ACHIEVE 99.9% INACTIVATION OF Giardia lamblia AND > 99.99% INACTIVATION OF ENTERIC VIRUSES FOR 0.4 mg/L OZONE

| | | Temperature (°C) | | | | | |
|---|---|---|---|---|---|---|---|
| Disinfectant | pH | 0.5 | 5 | 10 | 15 | 20 | 25 |
| Ozone (0.4 mg/L) | 6-9 | | | | | | |
| CT value | | 5 | 3 | 2.5 | 2.0 | 1.5 | 1.0 |
| Contact Time (min) | | 12.5 | 7.5 | 6.25 | 5 | 3.75 | 2.5 |

If the dissolved ozone residual can be raised to 0.5 mg/L, the contact times will be somewhat lower. If the ozone residual is lower (i.e., 0.3 mg/L), the contact time will be somewhat longer. If only a 1-log inactivation of Giardia is required, as when preozonation is practiced prior to filtration), the CT value (and therefore, the ozone contact time) required will be even lower (see Table IIB).

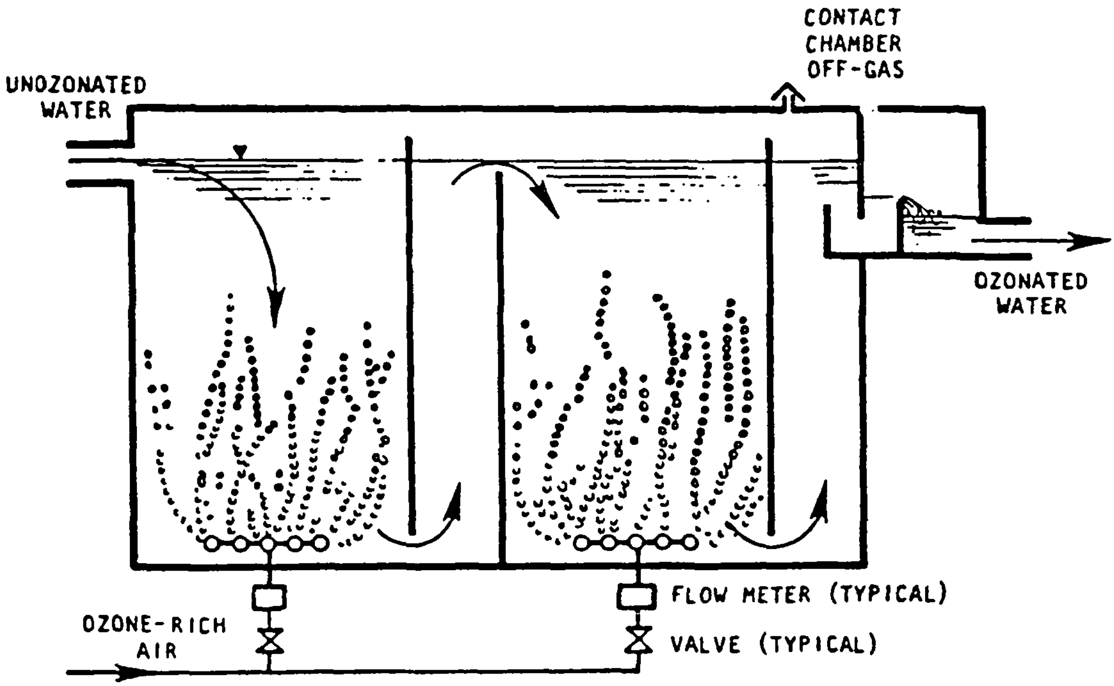

Figure 5. Two-compartment ozone contactor with porous diffusers.

Many current ozonation systems in the U.S. today are designed to optimize the oxidative capabilities of ozone, not necessarily to optimize ozone disinfection. In these instances it is customary to provide a single ozone contact chamber. If single contact chambers are used for ozone disinfection, and the residual ozone concentration is measured at the outlet of the contact chamber, how should the contact time be determined?

The initial response is to assume that the ozone residual concentration at the outlet is present throughout the contact chamber. Were this to be true, one would simply multiply the detention time in the contactor by the concentration of ozone in the water exiting the contactor to determine the CT value.

However, this assumption is incorrect. Considering only the first compartment of the 2-compartment ozone contactor in Figure 5, it must be realized that the water entering the upper part of the compartment contains no ozone and constantly exerts an ozone demand. Therefore it can be concluded that the upper portion of this compartment contains much less ozone than the lower portion. However, the ozonized water exits from the lower section with a measurable dissolved ozone residual.

It is clear from this reasoning that the true CT value of a single contact chamber is lower than that obtained by multiplying the detention time by the ozone concentration in the water exiting the chamber. As a first approximation only, one should assume that the average concentration of ozone throughout the contact chamber is, say, 50% of that measured at the outlet. But even this approximation may not be true.

If single ozone contact chambers are to be supplied, it is advisable to measure the dissolved ozone concentrations at various points in the chamber at the various water flow rates and ozone dosages with the actual water to be treated. In this manner, a CT value can be calculated which is closer to the true value.

It must be recognized that if ozone is employed early in the water treatment process to oxidize iron and manganese, and if the levels of iron and manganese are sufficiently high, copious amounts of brown/black precipitate will be produced. These insoluble materials will interfere with the measurement of a dissolved ozone residual, even though a significant residual may be present.

### vii. Factors Affecting the Disinfecting Efficiency of Ozone

It should be recognized that because ozone is such a powerful oxidizing agent, it is not particularly selective. In other words, if ozone is used early in the water treatment process, for example, to oxidize iron and manganese, or color, or tastes and odors, a high degree of disinfection also will be obtained. Conversely, if ozone is used after filtration for disinfection, it will also oxidize any easily oxidizable materials still present.

Ozone is affected little by changes in water temperatures or pH, and it does not react with water, except as noted earlier. Also, ozone does not react with ammonia at any significant rate, except above pH 9. However, ozone does have a short half-life in water, decomposing to oxygen at a rate dependent upon the water temperature. This means that ozone will not have a lasting residual in the distribution, and therefore normally cannot be employed as the secondary disinfectant. Although there are a number of European, Canadian, and even two U.S. water treatment plants which do use ozone as the secondary disinfectant, these are the exception rather than the rule. In those cases in which ozone is the last treatment step, a combination of five factors must occur simultaneously (Miller et al., 1978):

- cool water temperatures,
- clean and short distribution system,
- short residence time (< 12 hours)
- low levels of organics,
- no ammonia present.

In all other cases, a secondary disinfectant which provides a stable residual is added after ozone has been utilized as the primary disinfectant. One advantage of employing ozone as the primary disinfectant is that the oxidant demand of the water is satisfied simultaneously, which allows much lower dosages of chlorine, chlorine dioxide, or monochloramine to be utilized, normally less than 0.5 mg/L to provide a stable residual for the distribution system.

### viii. **Ozonation System Design**

Figure 6 illustrates the five basic components of an ozonation system which employs ambient air as the generator feed gas. The essential components include air preparation, electrical power supply, ozone generation, ozone contacting, and ozone contactor exhaust gas destruction. The amount of ozone produced by an ozone generator is affected by the physical characteristics of the equipment, the power supply to the ozone generator, the moisture content and dust content of the feed-gas, the temperature of the ozonized gas, and the oxygen content of the feed gas. Each of these factors will be discussed below.

#### Air Preparation

Ambient air must be dried to a maximum dew point (a unit of moisture content of air) of minus 60°C. Even drier gas is preferable (lower than -60°C). This sub-process must be designed conservatively, especially for warm, humid climates. Use of air having a dew point higher than -60°C will result in lower ozone production, foul the ozone production (dielectric) tubes or plates, and increase corrosion problems in the ozone generator unit and downstream equipment as well.

Air feed systems typically are classified by their operating pressure. The most common is a low pressure system, which operates at a pressure ranging from 69 to 103 kilopascals (kPa = 10 to 15 psig), although pressures up to 275 kPa (40 psig) have been reported when the pressure is reduced prior to the ozone generator. High pressure systems operate at pressures ranging from 480 to 690 kPa (70 to 100 psig), reduce the pressure prior to the ozone generator, and typically are used in small to medium sized applications. Either system may be used in conjunction with most ozone generators and with all of the contacting systems described.

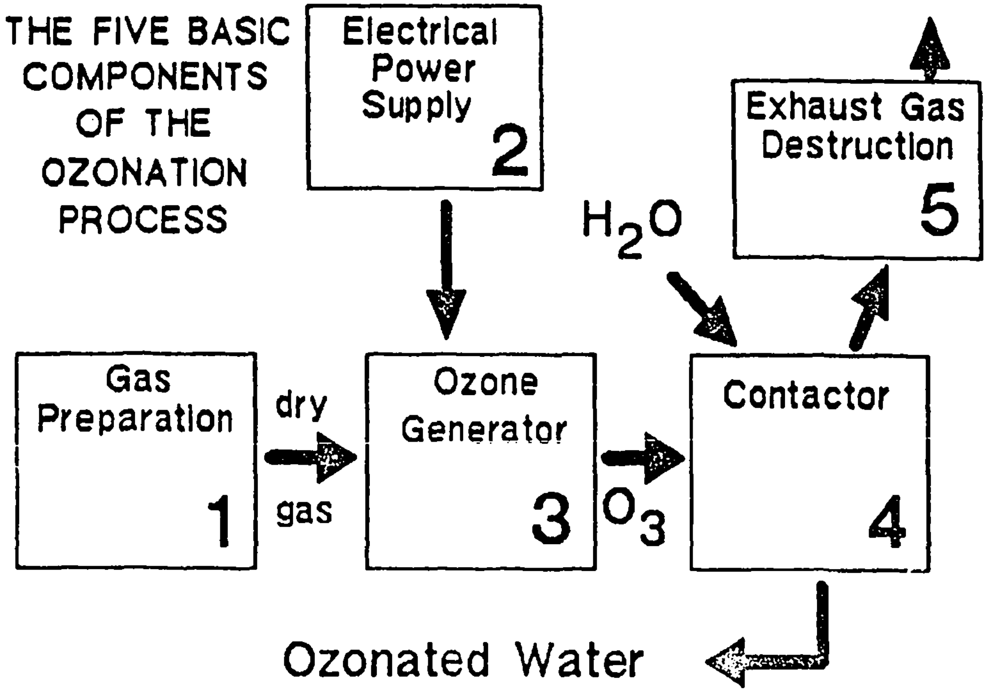

Figure 6. The five basic components of an air-fed ozonation system.

The decision to use a high or low pressure air preparation system often is based on a qualitative evaluation of potential maintenance requirements, in addition to the quantitative capital cost evaluation. Some of the issues to consider are listed below:

1. High pressure air pretreatment equipment generally has higher maintenance requirements for the air compressors;

2. High pressure air pretreatment equipment generally has lower maintenance requirements for the desiccant dryers.

3. High pressure air pretreatment equipment generally has a lower capital cost. At small to medium sized installations this lower capital cost may offset the additional maintenance required for the air compressors and associated equipment, such as filters for the oil-type compressors. The design engineer should investigate the potential maintenance associated with the high and low pressure systems rather than evaluating the design on the basis of capital cost alone.

Another type of air feed-gas treatment system is the "nominal pressure" system, which typically operates at a negative or in some cases a slightly positive pressure. This type of air pretreatment system is designed to operate in conjunction with aspirating turbine, injector, and/or Venturi type contactors, all of which create the partial vacuum necessary to draw ambient air through the air pretreatment and ozonation systems. Since ozone disinfection of drinking water involves maintenance of a specific ozone contacting time to attain the required CT value, this type of contacting will require higher energy expenditures than the positive pressure contactors (and positive pressure air pretreatment systems). Therefore, nominal pressure air pretreatment systems are not considered appropriate for drinking water disinfection.

Figures 7 and 8 are schematic diagrams showing low pressure and high pressure air feed gas pretreatment systems, respectively. Figure 7 illustrates a dual component process, showing desired flexibility for the equipment provided. The precompressor filters are provided to protect the air compressors from damage due to large particles. The air compressors typically are positive displacement, oil-less units. Positive displacement compressors are used in order to obtain constant air flow at variable operating pressures. Variable pressures often are encountered due to variable pressure losses in downstream equipment and processes such as filters and ozone contact basins. Oil-less compressors are used to eliminate oil contamination of the downstream desiccant dryer medium and ozone generator dielectrics. Liquid-seal and rotary lobe compressors have been used most frequently.

The compressors may be followed by an after-cooler or a refrigerant dryer. These components are depicted by dotted lines in Figure 7, which indicate that they are optional. Typically, either one or the other option is provided. These cooling mechanisms are used to remove moisture in the air at minimal operating expense.

The compressed, cooled air is directed to a predesiccant filter, which is used to remove dust and dirt particles greater than 3 to 5 microns in diameter. Particulate removal prior to the desiccant dryers reduces plugging in the desiccant medium.

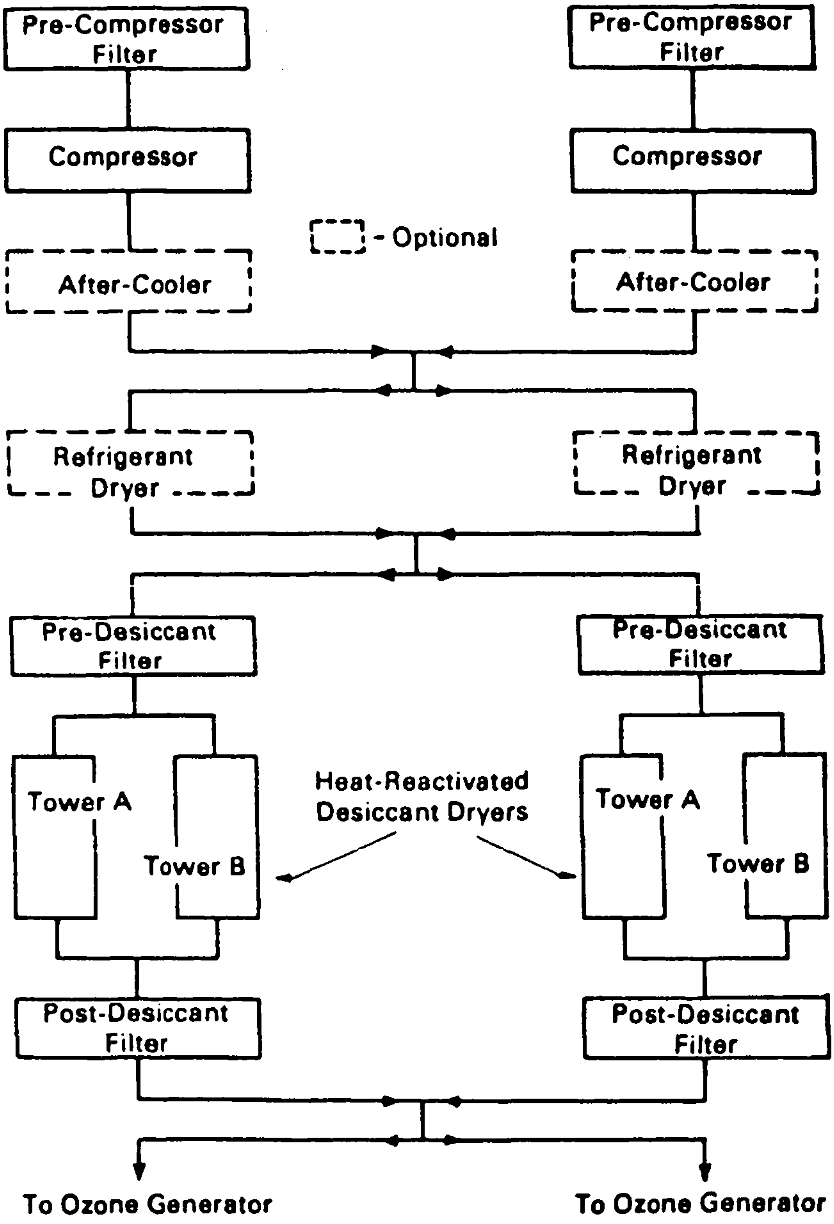

Figure 7. Example low pressure air feed-gas treatment schematic for ozone generation (U.S. EPA, 1986, p. 125).

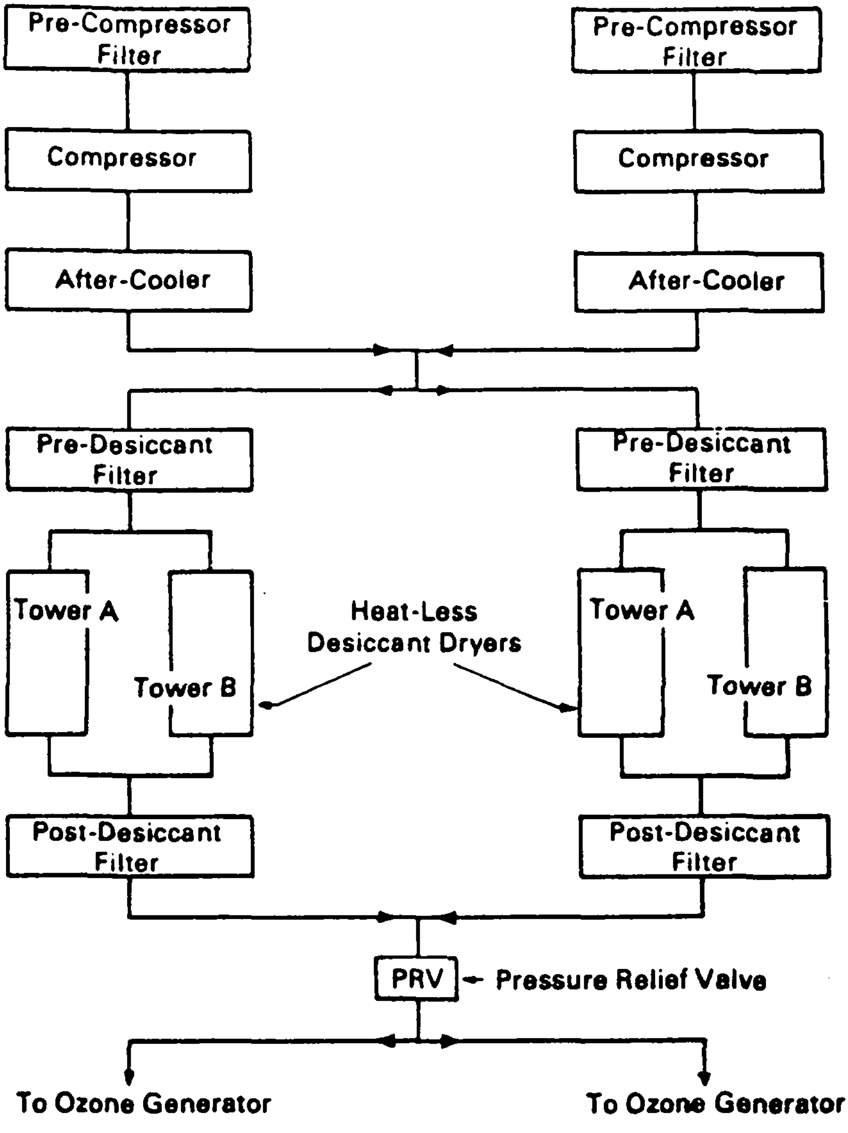

Figure 8. Example high pressure air feed-gas treatment schematic for ozone generation (U.S. EPA, 1986, p. 126).

Probably the most important component of the air treatment process is the desiccant dryer, which consists of two towers containing moisture-adsorbing media. One tower operates in the adsorption mode while the other tower is being regenerated. The low pressure system desiccant dryer uses heat for reactivation of the desiccant.

Post-desiccant filters are installed to remove particulates smaller than 0.3 to 0.5 micron in diameter. Two-stage filtration is preferred. The first stage filter removes particulates greater than 1 micron and the second stage removes particulates less than 0.3 to 0.4 micron in diameter.

In the high pressure air pretreatment system (Figure 8), the precompressor filters are used to remove larger particulates and protect the air compressors. These compressors typically are oil-less units; however, oil-seal compressors can be used if followed by extensive oil removal equipment.

Following the high pressure compressors, it is essential to provide after-coolers, to remove the heat of compression. The filter(s) before the desiccant dryer are used to remove particulates less than 3 to 5 microns in diameter when oil-less compressors are used. When oil-seal compressors are used, filtration to remove oil droplets less than 0.03 micron is provided.

The high pressure system desiccant dryer consists of two towers with moisture adsorbing media. One tower operates in the adsorption mode while the other is regenerating. Regeneration is accomplished without additional heat. Thus, the high pressure desiccant dryers are called heat-less units. The post-desiccant filters remove particulate matter less than 0.3 to 0.4 micron in diameter. The high pressure system also has a pressure reducing valve to regulate operating pressures in the ozone generator.

Air compressor, refrigerant dryer, and desiccant dryer design considerations are discussed in detail in U.S. EPA, 1986.

## Electrical Power Supply

Supply line voltage (220/440 V), or frequency in some cases, is varied to control the amount of ozone being generated and its rate of generation. Because these two parameters are varied in many ozone generation systems, the electrical power subunit can represent a proprietary product of the ozonation system supplier. As a result, the electrical power system must be specified as an integral power supply system specifically designed for the ozone generator to be supplied. In other words, the power system should be designed for and purchased from the ozone generating system supplier.

Because the ozone generator uses high voltage (> 10,000 V) and in some cases also high frequency electrical current (up to a maximum of 2,000 Hz), special electrical design considerations must be implemented. For example, special insulation must be provided for the electrical wire. A cool environment for the high voltage transformers should be provided, and the electrical transformers should be protected from ozone contamination due to minute ozone leaks which might occur on a periodic basis.

The electrical considerations for an ozone system should receive special attention. For example, a number of problems have been reported with dry-type potential transformers. Oil-cooled transformers apparently have performed more reliably. In view of the dependence of ozone generation on high frequency or high voltage electrical energy, the ozone generator supplier should be responsible for designing and supplying the electrical subsystems. However, the specifications should require that the frequency and voltage transformers be high quality units designed for ozone service. The ozone generator supplier should be requested to provide a record of successful electrical equipment performance.

Another item to consider in the design of an ozone generating system is the power factor. This is the ratio between the apparent power (kW) measured by a watt-hour meter and actual power (kVA) measured in terms of voltage and amperage. The relationship is shown by the equation:

$$\text{Power Factor} = \text{Apparent Power/Actual Power}$$

$$pf = kW/kVA$$

The power factor is UNITY when the voltage and current of an alternating current power supply are "in-phase" with each other, for example in a purely resistive circuit like a heating element. In a purely capacitive circuit, such as an ozone generator which has not reached the ionization potential of the dielectric, the voltage and current are 90 degrees out of phase. In this case, the power factor is ZERO. For a generator producing ozone, the voltage and amperage will be somewhere between 0 and 90 degrees out of phase; thus, the power factor will be less than 1.0. The actual power factor will vary depending upon the power supply to the ozone generator and the amount of electrical resistance developed within the electrical circuit.

The power factor may be corrected by installing inductors in the electrical circuit or by using the inductance created by the operation of motors in other areas of the treatment plant. However, caution must be exercised when using other plant equipment for power factor correction, because of the variable operating conditions of the equipment from hour to hour and from day to day. The inductance of other equipment should be used only to control the low power factor of the ozone generator when consistent equipment operation can be assured.

An operating ozone generator can decrease the power factor to 0.3 to 0.5, depending on the generator setting. Corrections normally will be cost-effective, since utilities that supply electrical power typically impose penalties for a low power factor.

## Ozone Generators

The most common commercially available ozone generators can be classified as follows:

- horizontal tube; one electrode water-cooled,
- vertical tube; one electrode water-cooled,
- vertical tube; both electrodes cooled,
- plate; water- or air-cooled.

The operating conditions of these ozone generators can be subdivided as follows:

- low frequency (50/60 Hz), high voltage (> 20,000 V),
- medium frequency (600 Hz), medium voltage (< 20,000V),
- high frequency (> 1,000 Hz), low voltage (< 10,000 V).

Currently, low frequency - high voltage units are most common, but recent developments in electronic circuitry are resulting in higher frequency units (and lower voltages) being used.

To determine the amount of ozone required to provide disinfection, the following steps are recommended:

1. Estimate the initial ozone demand of the water at the point of entry into the first chamber of the ozone contactor. The initial ozone demand is that quantity of ozone necessary to develop a stable residual ozone concentration at the outlet of the first contact chamber. In most ozone disinfection processes, the ozone residual attained is 0.4 to 0.5 mg/L, and the initial ozone demand is between 1 and 6 mg/L, depending upon the water quality at this point.

2. If the initial ozone demand is estimated, assume a 90% ozone transfer efficiency for the 2-chamber bubble diffuser contactor.

3. An additional amount of ozone will be required in the second chamber of the ozone contactor to maintain the residual of ozone for the appropriate period of time to attain the necessary CT value. Assume this amount of additional ozone will be 50% of that applied in the first chamber.

4. Determine the peak water flow through the plant, and from this, calculate the peak ozone requirement.

In operating ozone treatment systems, a single generator designed for peak use is never installed, in order to minimize energy costs during operation, provide backup capability, and to facilitate maintenance operations. The minimum production rate from an ozone generator is 10 to 25 percent of its maximum production capability. On the other hand, the most cost-effective production rate of an ozone generator occurs at 60-70% of its maximum production rate.

Therefore, if the treatment plant requires, say, 100 lbs/day of ozone during normal production, and 150 lbs/day for peak operation, it is cost-wise to purchase three 60 lbs/day generators, and operate all three at about 65% of their capacity for normal production. This approach allows satisfying the occasional peak ozone demands, provides one standby generator during normal flows, and allows the down generator to be maintained on a periodic schedule.

## Ozone Contactors

The different types of contactors have been discussed earlier. Selection of the specific type of contactor should be based upon the specific type of ozonation task contemplated. For disinfection, the most commonly used contactor is the two-chamber, porous plate or porous tube diffuser contactor shown in Figure 5. Housings for such contactor systems normally are constructed of concrete.

## Destruction of Excess Ozone

Ozone destruction is used to remove excess ozone in a contact basin off-gas prior to venting or prior to recycle or reuse of the exhaust gas. Safety is the major consideration. The maximum ambient air concentration currently allowed by the OSHA exposure of human beings over an 8-h working day is 0.0002 g/m$^3$ (0.1 ppm by volume). This concentration is significantly less that the ozone concentrations in contactor exhaust gases, normally greater than 1 g/m$^3$ (500 ppm by volume).

The primary methods for treating excess ozone in the exhaust gases are: thermal destruction (300-350°C for 3 sec), thermal/catalyst destruction, and catalyst destruction (metal catalysts or metal oxides). Moist granular activated carbon is used quite extensively in small scale European ozonation systems generating g/h quantities of ozone (< 2 mgd water supplies; large public swimming pools, etc.), but is not recommended (U.S. EPA, 1986, p. 137) for this purpose.

The most favored procedure currently involves passing the contactor exhaust gases through a catalytic ozone destruction unit, which contains a proprietary catalyst system based on manganese dioxide. Excess ozone is converted to oxygen, which may be discharged safely to the ambient atmosphere.

Ozone contactor exhaust gases are treated in this manner, rather than drying or recirculating through the ozone generator for economic reasons. It is more cost-effective to dry ambient air than to dry the wet air exiting the ozone contactor.

## Materials of Construction

Care must be taken in selecting materials of construction for those portions of the ozonation system in direct contact with either "dry" (before the contactor) or "wet" (after the contactor) ozone-containing gas. While reinforced concrete is an appropriate material for ozone contactors, the ozone-containing gas piping system should be 304-L or 316-L stainless steel for dry and wet services, respectively.

## Monitoring the Ozonation System Operation

Equipment should be provided to monitor the operation of the components of the system. The minimum degree of instrumentation, all of which can be provided by the ozone equipment supplier as part of the package units, is as follows:

- Gas pressure and temperature devices at key points in the air preparation system. Simple pressure gauges and mercury thermometers will suffice.
- Continuous monitoring of the dew point measuring device to determine the moisture content of the dried air feed gas to the ozone generator. High dew point indications should be designed to sound an alarm and shut down the generator. Equipment for calibration of the dew point monitor should be provided as well.
- Means of measuring inlet/discharge temperatures of the ozone generator coolant medium (water and/or oil, or air) is required, as is a means of determining whether coolant is

actually flowing through the generator. An automatic system shutdown should be provided if coolant flow is interrupted or if its discharge pressure exceeds specified limits.

- A means of measuring flow rate, temperature, pressure, and ozone concentration of the ozone-containing gas discharged from the ozone generator is required to determine the ozone production rate.
- A means of measuring the power input to the ozone generator is required.

### Ozone Equipment Suppliers

Table XXIV is a listing of the major suppliers of corona discharge ozone generation equipment in the United States (Source: International Ozone Association, Pan American Committee, Norwalk, CT). Each of these suppliers provides the total ozonation system, including electrical power supply, air preparation equipment, contacting apparatus, and contactor off-gas destruction devices, as well as the appropriate monitoring and automation equipment.

## ix. Costs of Ozonation Systems

### Equipment Costs

These will include estimates for ozone generation equipment and ozone contacting systems, both of which are supplied by the ozone systems manufacturers. Water supply systems treating 0.5 mgd and less will require a daily ozone generation capacity from three to 21 pounds, and will be able to dose ozone at average levels of up to 3-5 mg/L. At these production levels, ozone normally will be generated from dried air, not oxygen, in order to avoid the costs of oxygen generation, recovery and recycle equipment.

As mentioned earlier, the new 540-mgd Los Angeles drinking water plant uses oxygen as the feed gas to the ozone generators. A new German ozone generator, currently marketed in the U.S. by Capital Controls Co. (the CAPOZON system) is designed to generate ozone from pure oxygen, in small diameter dielectric tubes. Because of this new design, this system is capable of generating unusually high concentrations of ozone (14%) in oxygen. This system may find application for drinking water treatment plants in the future.

Ozonation equipment to be purchased includes the following:

- air preparation equipment (drying and chilling)
- ozone generator
- ozone contactor
- ozone destruction unit
- instrumentation and controls

TABLE XXIV. MAJOR U.S. OZONATION SYSTEMS SUPPLIERS

| Name | Address |
|---|---|
| BBC Brown Boveri Inc. | 1460 Livingston Ave., North Brunswick, NJ 08902 |
| Capital Controls Co., Inc. | Box 211, 3000 Advance Lane, Colmar, PA 18915 |
| Emery Chemicals Inc. | 4900 Este Avenue, Cincinnati, OH 45232 |
| Gould & Eberhardt Industries | P.O. Box 190, Sutton Road, Webster, MA 01570 |
| Griffin Technics Corp. | 178 Route 46, P.O. Box 330, Lodi, NJ 07644 |
| Hankin Environmental Systems | 71 Route 206 South, Somerville, NJ 08876 |
| Infilco Degremont Inc. | P.O. Box 29599, 2828 Emerywood Parkway, Richmond, VA 23229 |
| Mitsubishi, Electric Sales, MEDAMA, Inc. | 5757 Plaza Drive, Cypress, CA 90630-0007 |
| Ozone Research and Development Corporation | 3840 North 40th Avenue, Phoenix, AZ 85019 |
| PCI Ozone Corporation | One Fairfield Crescent, West Caldwell, NJ 07006 |
| Trailigaz of America | 1 Jenkintown Plaza, 211 West Avenue, Suite 210, Jenkintown, PA 19046 |
| Welsbach Ozone Systems Inc., Division of Polymetrics, Inc. | 101 Nicholson Lane, San Jose, CA 95134 |

For generation of large quantities of ozone (100 lbs/day and higher), approximately $1,200 per pound of ozone generation capacity per day will be required to procure the air preparation, ozone generation, and contacting equipment. Ozone destruction and instrumentations and controls will be in addition to this figure.

For smaller quantities of ozone, costs will be higher, but will vary significantly from site to site.

For the small production quantities of ozone required by small water treatment plants serving less than 10,000 persons per day (three to 21 pounds per day), all items except the contactor can be assembled into a single skid-mounted unit. If the contactor selected is the turbine type, it also can be included in the skid-mounted assembly unit.

Diffuser contactors for small ozonation systems generally are constructed of polyvinyl chloride (PVC) pipe standing on end, or of fiberglass reinforced plastic (FRP) tanks. A contact chamber containing diffusers should be approximately 18-ft high, providing a water depth of 16-ft and a detention time of 10-20 minutes, to attain the appropriate CT value required for 99.9% inactivation of Giardia lamblia cysts and/or 99.99% inactivation of enteric viruses. These conditions will maximize the transfer of ozone from gas phase to aqueous solution when employing diffuser contacting systems.

Tables XXV and XXVI list equipment cost estimates obtained from two ozonation systems suppliers in 1982, for various daily ozone generation rates. Ozone supplier A (Table XXV) provided estimates for ozone dosages provided estimates for ozone dosages of 3 and 5 mg/L at water flow rates of 500,000 gal/day, 350,000 gal/day, and 180,000 gal/day. This breakdown shows that equipment costs for air pretreatment and ozone generation capacity available from this supplier depend upon the dosage required at a particular water flow rate. In addition, the size (and cost) of the ozone destruction units required also varies, as does the power requirement to operate the total ozonation system.

Ozone Supplier A can provide four monitors with his system. All are optional, but all are recommended for optimal performance and minimal labor and downtime. These will monitor:

- the dew point in the air preparation unit,
- ozone output of the generator,
- ozone in the plant ambient air (in case of leaks),
- dissolved ozone residual in the water.

The cost of these four monitors is constant at $15,000, regardless of system size in the range shown in Table XXVI (5 to 21 pounds per day).

TABLE XXV. COSTS OF OZONATION EQUIPMENT FOR SMALL WATER SUPPLY SYSTEMS (Company A - May 1982)

| Size of water supply | 500,000 gpd | | 350,000 gpd | | 180,000 gpd | |
|---|---|---|---|---|---|---|
| Maximum dosage of ozone (mg/L) at peak flow | 5 | 3 | 5 | 3 | 5 | 3 |
| Daily ozone requirement (lbs) | 21 | 14 | 14 | 7 | 7 | 5 |
| Contact chamber diameter (14 ft high, 4 compartments, 4 diffusers, Derakane fiberglass reinforced plastic) | 6 ft | 6 ft | 5 ft | 5 ft | 4 ft | 4 ft |
| EQUIPMENT COSTS | | | | | | |
| Air preparation + ozone generation unit | $31,500 | $25,000 | $25,000 | $22,000 | $22,000 | $19,500 |
| Contact chamber with diffusers | $11,500 | 11,500 | 10,200 | 10,200 | 9,900 | 9,900 |
| Monitoring Instrumentation | | | | | | |
| 1) Ozone in generator product<br>2) Ozone in ambient plant air<br>3) Ozone dissolved in water<br>4) Dew point monitor in air preparation unit | $15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 |
| Ozone Destruction Unit | $6,700<br>(10 cfm) | 5,000<br>(7 cfm) | 5,000<br>(7 cfm) | 4,200<br>(3 cfm) | 4,200<br>(3 cfm) | 4,200<br>(3 cfm) |
| TOTAL EQUIPMENT COSTS | $64,700 | $56,500 | $55,200 | $51,400 | $51,100 | $48,600 |
| Power requirement kWh | 13.3 | 10.1 | 10.1 | 5.0 | 5.0 | 3.65 |

TABLE XXVI. COSTS OF OZONATION EQUIPMENT FOR SMALL WATER SUPPLY SYSTEMS (Company B - May 1982)

| Flow Rate | 0.1 mgd | | 0.2 mgd | | 0.3 mgd | | 0.4 mgd | | 0.5 mgd | |
|---|---|---|---|---|---|---|---|---|---|---|
| Maximum ozone dosage, (mg/L), at peak flow | 3 | | 3 | | 3 | | 3 | | 3 | |
| Daily ozone requirement (lbs/day) | 3 | | 6 | | 7 | | 12 | | 14 | |
| Equipment Costs | LP** | HP*** | LP | HP | LP | HP | LP | HP | LP | HP |
| Air preparation + ozone generator* | - | $17,500 | $33,200 | $30,200 | $38,500 | $35,500 | $43,000 | $40,000 | $49,800 | $46,800 |
| Power requirements (kWh/lb of O3 generated) | 10.5 | 20 | 10.5 | 13.5 | 10.5 | 13.5 | 10.5 | 13.5 | 10.5 | 13.5 |
| Ozone contactor with diffusers | $8,500 | | $12,000 | | $16,000 | | $21,000 | | $29,000 | |
| Ozone Monitors | $4,000 | | $4,000 | | $4,000 | | $4,000 | | $4,000 | |
| - O3 generation**** | or 2,000 | | or 2,000 | | or 2,000 | | or 2,000 | | or 2,000 | |
| - O3 room or contact chamber exhaust | 2,200 | | 2,200 | | 2,200 | | 2,200 | | 2,200 | |
| - dew point | 3,500 | | 3,500 | | 3,500 | | 3,500 | | 3,500 | |
| TOTAL EQUIPMENT COSTS | - | $33,700–35,700 | $54,900–52,900 | $51,900–49,900 | $64,200–62,200 | $61,200–59,200 | $73,700–71,700 | $70,700–68,700 | $88,500–86,500 | $85,500–83,500 |

* includes air preparation, ozone generation, ozone destruction and system controls.

** air preparation unit includes air filters or separators, compressor delivering air at 8-12 psig to a refrigerative cooler and a dual tower desiccant dryer.

*** same as LP air preparation system, except compressor delivers air at 80-120 psig. HP system takes less space requires less maintenance, but requires more energy.

**** $4,000 instrument is an automatic, continuous reading in-line monitor.
$2,000 instrument is not automatic and utilizes wet chemistry.

Table XXVI shows similar data for Ozone Supplier B. In this case, equipment costs are presented for water flows of 100,000, 200,000, 300,000, 400,000, and 500,000 gal/day. Average ozone dosages are taken as 3 mg/L, and the daily ozone output required varies from 3 lbs/day for treating 100,000 gal/day to 15 lbs/day for treating 500,000 gal/day.

Ozone Supplier B offers two types of air preparation equipment, however, and estimates are presented for each. One type operates at high pressures (80-120 psig), and the other at low pressures (8-12 psig). The high pressure air treatment units are lower in capital cost, but require more energy for their operation.

Ozone Supplier B does not normally provide a residual dissolved ozone monitor, but offers two types of monitor for ozone output from the generator. The automatic, in-line continuous reading monitor costs $4,000; the non-automatic monitor requires wet chemistry determinations to develop data at some period of time after the sample has been taken, and costs $2,000.

Therefore, cost data presented in Table XXVI vary by the differences between costs for high and low pressure air preparation equipment, and by the costs of the two ozone generator monitors.

In 1987, Ozone Supplier A estimated that the cost for a 5-lb/day ozone generator, sufficient to treat 180,000 gal/day at an applied ozone dosage of 3 mg/L, to be $20,500. This confirms that costs for ozone generation equipment in 1983 are still current, for the smaller water treatment plants.

## Installation Costs

Costs for installation of the ozonation equipment include labor, and material costs for piping water to and from the ozone generators (if they are water cooled), for piping ozone-containing air to the contactor chamber, for piping water to and from the contactor, and for piping contactor off-gases to and from the ozone destruction unit. Electrical wiring costs also must be considered in these costs. Ozonation equipment suppliers contacted advise that for production of up to about 30 lbs/day of ozone, installation costs will be roughly the same, and will average 15% to 25% of the equipment costs of the largest units estimated in Tables XXV and XXVI. The actual figures for the two equipment suppliers then become:

| Supplier | Cost of Equipment (500,000 gpd plant) | Installation Cost (15% to 25%) |
|---|---|---|
| A | $64,700 | $ 9,705 - $16,175 |
| B | $85,000 | $12,750 - $21,250 |

## Housing Costs

The power supply, air preparation equipment, ozone generation equipment, and turbine contacting units can be installed relatively easily, in areas on the order f 10 x 17 feet. However, diffuser contacting units are tall (18 feet) and bulky, and normally are installed outside existing buildings (above ground) or underground inside buildings being constructed. Alternatively, a 170 $ft^2$ Butler building can house the ozonation system, except for above-ground diffuser unit. Such a building costs about $6,000.

## Operation and Maintenance Costs

Operating costs for ozonation systems vary, and depend upon a number of factors:

- method of air preparation,
- method of cooling the generator (water or air),
- if water-cooled, the amount of refrigeration required for cooling water,
- method of contacting,
- dosage of ozone required,
- pumping of generator coolant,
- method of contactor off-gas destruction.

Air Preparation: High pressure versus low pressure, versus subatmospheric pressure desiccant system with or without addition of air chiller.

Ozone Generator Cooling: Air versus water. If water, the amount of cooling required. In northern climates, water produced at the plant generally is cold enough to serve as the generator coolant the year round. In southern climates, generator cooling water must be refrigerated most, if not all, of the year.

Method of Contacting: Diffuser contactors require no added energy. Ozone/air mixtures normally are generated under a sufficient pressure to overcome the head of 16 feet of water. On the other hand, turbine diffusers require energy for their operation, but take up much less space than diffuser contactors. For disinfection with ozone, however, the appropriate reaction time must be provided after initial contacting has been achieved to attain the appropriate CT value to assure inactivation of Giardia lamblia cysts and/or enteric viruses.

Contactor Off-Gas Destruction: Thermal versus catalytic destruction. Operating costs of these techniques vary.

Maintenance material requirements are for periodic equipment repair and replacement of parts. Air preparation systems contain air prefilters which must be replaced frequently. Tube-type ozone generators normally are shut down once per year for cleaning of the tubes and other general maintenance. This can require several man-days of time, depending upon the number of ozone generators in the system. Spare parts normally consist of replacement tubes, which can be broken during cleaning, or which can deteriorate after years of operation at high voltages.

Labor requirements are for periodic cleaning of the ozone generation apparatus, annual maintenance of the contacting basins, and day-to-day operation of the generating equipment (average 0.5 h/day).

Operating and maintenance costs for equipment of Ozone Suppliers A and B are summarized in Table XXVII. Also included are building heating costs (which are taken to be the same up to 0.5 mgd) and costs for maintenance materials and O&M labor. There are no chemicals costs related to ozone generation, except for periodic changing of desiccant in air preparation systems (normally after 10 years of use).

Electrical energy is a major component of operating costs, representing 26% to 43% of total O&M costs at small plants (0.1 mgd) increasing to 59% to 65% at the larger plants (0.5 mgd).

Building energy costs (which are approximately the same for all small size plants up to 0.5 mgd) include energy costs for heating, lighting, and ventilation. Labor costs (which are independent of the plant sizes listed -- 0.1 to 0.5 mgd) account for 54% to 70% of total O&M costs at the small plants, but only 30% to 36% at the 0.5 mgd plant.

## Summary Statement Regarding Costs for Ozonation Systems

Because of the many differences in methods of air pretreatment, ozone contacting, contactor off-gas destruction, monitoring, and other operational parameters, equipment costs given above should not be considered as more than general guidelines. Vendor quotes should be obtained at the time ozone is being considered by the small water supply system.

It should be noted that vendor quotes obtained for estimating purposes are likely to be somewhat higher than firm bids made to specifications. This is because the market for ozonation systems currently is quite competitive, and suppliers usually bid their best prices when responding to clear specifications.

TABLE XXVII. OPERATING AND MAINTENANCE COSTS FOR SMALL OZONE SYSTEMS APPLYING 3 mg/L DOSAGE

| Water Flow Rate (mgd) | Electrical Energy (kWh/yr) | | | | | Labor | | |
|---|---|---|---|---|---|---|---|---|
| | Building* | Process | Total | x $0.07/kWh = | Maintenance Material | Labor (hrs/yr) | x $10/hr = | Total Cost ($/yr) |
| **Supplier A** | | | | | | | | |
| 0.18 | 6,570 | 6,661 | 13,231 | $ 926 | $120 | 250 | $2,500 | $ 3,546 |
| 0.35 | 6,570 | 12,775 | 19,345 | $1,354 | 200 | 250 | 2,500 | 4,054 |
| 0.50 | 6,570 | 51,611 | 58,181 | $4,073 | 300 | 250 | 2,500 | 6,873 |
| **Supplier B** (High Pressure Air Preparation) | | | | | | | | |
| 0.10 | 6,570 | 21,900 | 28,470 | $1,993 | $120 | 250 | 2,500 | $ 4,613 |
| 0.20 | 6,570 | 29,565 | 36,135 | $2,529 | 120 | 250 | 2,500 | 5,149 |
| 0.30 | 6,570 | 34,493 | 41,063 | $2,874 | 200 | 250 | 2,500 | 5,574 |
| 0.40 | 6,570 | 59,130 | 65,700 | $4,599 | 250 | 250 | 2,500 | 7,349 |
| 0.50 | 6,570 | 68,985 | 75,555 | $5,289 | 300 | 250 | 2,500 | 8,089 |

* Estimated from data of Hansen et al. (1979)

### c. Ultraviolet Radiation

Much of this discussion is taken from U.S. EPA, 1983, and 1986.

The effectiveness of UV radiation as a bactericide and virucide has been well established. It is a physical disinfecting agent compared to the chemical disinfectants, chlorine, chlorine dioxide, ozone, and monochloramine. Radiation at a wavelength of 254 nm penetrates the cell wall and is absorbed by the cellular nucleic acids. This can prevent replication and cause death of the cell. Since UV radiation is not a chemical agent, no toxic residual can be produced. Although certain chemical compounds can be altered by the radiation, the energy levels used for disinfection are far too low for this to be a significant cause for concern.

Major advantages of UV radiation are its simplicity, lack of impact on the environment and aquatic life, and minimal space requirements. Required contact times are very short, on the order of seconds rather than minutes. The equipment is simple to operate and maintain, but fouling of the quartz sleeves or Teflon tubes must be dealt with on a regular basis. Fouling normally is handled by mechanical, sonic, or chemical cleaning. High concentrations of suspended solids, color, turbidity, and soluble organic matter in the water can react with or absorb the UV radiation, reducing the disinfection performance.

#### i. General Description of the UV Process

Disinfection by UV radiation relies on the transference of electromagnetic energy from a source (lamp) to organism cellular material (specifically the cell's genetic material). The lethal effects of this energy result primarily from the cell's inability to replicate. The effectiveness of this radiation is a direct function of the quantity of energy, or dose, absorbed by the organism. This dose is described by the product of the rate at which energy is delivered, or intensity, and the time to which the organism is exposed to this intensity.

The primary artificial source of UV energy, at present, is the low pressure mercury arc lamp. It is almost universally accepted as the most efficient and effective source for disinfection systems application. The primary reason for its acceptance is that approximately 85% of its energy output is nearly monochromatic at the wavelength of 253.7 nm, which is within the optimum wavelength range of 250 to 270 nm for germicidal effects. The lamps are long [standard lengths are typically 0.75 and 1.5 m (2.5 and 4.9 ft) arc lengths] thin tubes [typically 1.5 to 2 cm (0.6 to 0.8 in) in diameter]. The radiation is generated by striking an electric arc through mercury vapor; discharge of the energy generated by excitation of the mercury results in the emission of the UV radiation.

The UV demand of a water is quantified by a spectrophotometric measurement at the key wavelength of 253.7 nm; this expresses the absorption (or transmittance) of energy per unit depth. The output is absorbance units/cm, or a.u./cm. The percent transmittance can be determined from this unit by the expression:

$$\% \text{ Transmittance} = 100 \times 10^{-(a.u./cm)}$$

The term most often used for design purposes is the UV absorbance coefficient, $\alpha$, expressed in base e:

$$\text{UV absorbance coefficient, } \alpha = 2.3\ (a.u./cm)$$

The unit for $\alpha$ is $cm^{-1}$.

A second major concern is the provision of adequate exposure time to the microorganisms in order to meet the dose requirement at a given intensity. The key is to have plug flow through the system, such that each flow element resides in the reactor for the same amount of time. Perfect plug flow is not possible to achieve, of course. Some dispersion will exist, such that there will be a distribution of exposure times about the ideal, theoretical exposure time. A design objective is to minimize this distribution.

The basic premise to understand is that the UV radiation must be absorbed before it can have a disinfecting effect. Photochemical damage occurs to the deoxyribonucleic acid (DNA) macromolecules which interferes with the ability of the cells to replicate. Cell death following UV radiation is almost entirely attributable to the photochemical damage of these compounds.

On the other hand, if the amount of radiation received by the organism is not a lethal dose, but only damaging, photoenzymatic repair can occur, and the effects of the UV radiation can be reversed. The phenomenon has been termed "photoreactivation". This repair mechanism is unique to UV radiation, but is not universal, and there is no clearly defined delineation of characteristics which suggest which species would have the ability to repair and which would not.

The enzymatic mechanism generally involved in photoreactivation requires subsequent (or concurrent) exposure to light at wavelengths between 300 and 500 nm. Such light is available in sunlight and in most incandescent and fluorescent light sources.

Therefore, to assure that disinfection occurs with no chance for photoreactivation, attention must be paid to designing the UV disinfecting system to provide sufficient UV dose for an appropriate period of time. As a general rule of thumb (U.S. EPA, 1986, p. 215), if a 3-log reduction of microorganisms is required to meet the disinfection criteria, the system should be designed to provide a 4-log reduction, to account for the effect of photoreactivation.

Table XXVII lists some of the major suppliers of UV disinfection equipment for water treatment systems.

TABLE XXVII. MAJOR SUPPLIERS OF UV DISINFECTION EQUIPMENT

| Name | Address |
|---|---|
| Aquafine Corp. | 25230 W. Ave Stanford, Valencia, CA 91355 |
| Aquionics Inc. | 21 Kenton Lands Road, Box 18395, Erlanger, KY 41018 |
| Atlantic Ultraviolet | 250 Fehr Way, Bay Shore, NY 11706 |
| Ultra Dynamics Corp. | 1631 Tenth St., Santa Monica, CA 90404 |
| Ultraviolet Purifications | 299 Adams St., Bedford Hills, NY 10507 |
| Ultraviolet Technology Inc. | 8930 Osage Ave., Sacramento, CA 95828 |

### ii. UV Disinfection System Design

In all, the design of a UV system must accommodate a few simple considerations:

- satisfy the UV demand of the water,
- maximize the use of the UV energy being delivered by the lamps, and
- provide the conditions which encourage plug flow.

UV lamps can be suspended outside the liquid to be treated or submerged in the liquid. In either design, the intent is to get the energy into the liquid as efficiently as possible. Typically, if the lamp is to be submerged in the liquid, it is inserted into a quartz sleeve to minimize the cooling effects of the water. Lamps can be placed in the liquid with the lamp perpendicular to the direction of water flow. Other configurations may have the lamp parallel to the flow, or the lamp may be suspended above the flowing liquid. As the lamp emits radiation, the intensity will attenuate as the distance from the lamp increases; this is simply due to the dissipation or dilution of the energy as the volume that it occupies increases. A second attenuation mechanism involves the actual absorption of the energy by chemical constituents contained in the water. This, analogous to the chlorine or ozone demands, is the "UV demand" of the water. The key points to be addressed when evaluating or specifying the design of a UV reactor are as follows:

1. Residence Time Distribution (RTD). This should be constructed at a number of flow conditions for an existing system. It should also be required when specifying commercial systems. The RTD provides key information on the actual or anticipated hydraulic behavior of a reactor.

2. Plug Flow. As a guideline, an aspect ratio greater than 15 should be incorporated into the reactor design. Maintenance of plug flow within a reactor will be influenced by the approach and exit conditions. The design should have minimal disturbances at the inlet and exit planes of the lamp battery. Directional changes in the flowpath would best be made outside of the lamp battery.

3. Dispersion Number: A key goal is to minimize the dispersion number, d. A design goal should be to have d between 0.02 and 0.05. This would be representative of a plug flow reactor with low to moderate dispersion. This can be accomplished by increasing the product of ux (u = velocity of water as it travels through the reactor, in cm/sec; x = the average distance traveled by an element of water while under direct exposure to UV radiation, in cm), even in a system with a relatively high dispersion coefficient.

The designer should be aware, however, that extended lengths and higher velocities will cause higher head losses. In certain situations, some adjustment of the dispersion number may be necessary in order to meet specific head loss requirements.

4. Turbulence: Radial turbulence is necessary due to the nonuniform intensity field. The reactor design should induce an estimated Reynold's Number greater than 6,000 at minimum flow. If possible, it would be beneficial to confirm the laminar/turbulent flow transition velocity by direct head loss measurements on the lamp battery.

5. Head Loss: Direct measurements should be required for full-scale modules or scaleable pilot units as part of commercial equipment specifications. These should be determined over a wide velocity range and should exclude entrance and exit losses.

6. Effective Volume: Maximal use of the reactor lamp battery is essential to keep the process cost-effective. This will be related directly to the reactor's inlet and outlet design. The goal must be to have equivalent velocities at all points upon entering and upon exiting the lamp batteries. Stilling walls (perforated baffles), and weirs should be incorporated into reactor designs to assure this. Guidelines for specifying commercial equipment should require the ratio $\theta/T$ to be greater than 0.9 and/or the ratio of $t_p/T$ to be greater than 0.9.

### iii. Estimating the Average Intensity in a UV Reactor

The second element of UV dose, after time, is the intensity of energy during the exposure time. Intensity is the rate (or flux) of delivery of photons to the target. In UV process design models, the rate of bacterial inactivation is described as a function of the intensity. By this fact, it becomes important to be able to quantify the intensity in a given system. The intensity in a reactor is a function of the UV source (output), the physical arrangement of the source relative to the water (the arrangement of the lamps and their placement in or out of the liquid), and the energy sinks present which will attenuate the source output before it can be utilized for disinfection processes.

Lamps used in UV disinfection systems generally have lengths of approximately 0.9 and 1.6 m. The arc length defines the active, light-emitting portion of the lamp (0.75 m and 1.5 m, respectively). The diameter of the lamp is small, typically 1.5 and 1.9 cm. The lamp envelope is made of fused quartz or other highly transparent (to the 253.7 nm wavelength) glass material, such as Vycor.

In the quartz systems, the individual lamps are sheathed in quartz sleeves only slightly larger in diameter (2.3 cm) than the lamp, and the entire lamp/quartz bundle is submerged in the flowing liquid. In systems where the water does not contact the quartz or lamp surface, separate conduits carry the waters. The conduits are translucent to the UV light, with the lamps placed near the outside conduit wall.

## iv. Water Quality Considerations in the Design of a UV Disinfection System

Without question, a major element in the effective design of a UV disinfection system is a clear and concise understanding of the characteristics of the water to be treated. These are directly related to the degree of pretreatment the material will receive before the disinfection step and will affect the sizing and performance of the disinfection system. Pretreatment ranges from very minimal, as in the case of a groundwater which requires no treatment other than disinfection, to full conventional treatment of a polluted surface water.

The four water quality parameters which most affect the design or performance of a UV disinfection system are the flow rate, initial microorganism density, suspended solids (or turbidity), and the UV absorbance of the water at the point of application of UV radiation.

1. Flow Rate: The flow rate is set by design of the main plant and projections of the hydraulic load to the plant. In evaluating the design requirements for the disinfection process, some consideration should be given to the equalization effects of the treatment processes before disinfection. This can have an effect on the sizing of the UV system.

Flow estimates should be for the design year of the plant. There should be some knowledge of the progressive increase in the flows through the design life of the plant in order to determine if the system can be phased in by the addition of modules as the demand increases. Some consideration also should be given to the hydraulic load to the unit.

For disinfection, average flows are not critical to the design sizing; rather they are important to estimating average utilization of the system for operation and maintenance needs. Peak flows should be used for sizing, particularly reflecting diurnal variations.

2. Initial Microorganism Density: The performance of a UV disinfection unit is related directly to the initial density of the indicator organisms. This is not a parameter which is generally monitored at a treatment plant, particularly one already employing chlorine for disinfection. In the case of disinfection by UV, however, it is critical. Performance is given by the log of the survival ratio, $N/N_0$, or by the number of "logs" the density is reduced.

3. Suspended Solids (Turbidity): From the development of the UV disinfection model, it is clear that the occlusion of bacteria in the particulates will have a significant effect on the design of a UV system. It is recommended (U.S. EPA, 1986) that the turbidity measurement be used as the primary indicator to quantify these particulates.

4. UV Absorbance: The one parameter which is solely in the venue of UV disinfection is the UV "demand" of the water. Some organic and inorganic compounds in the water may absorb energy at the 153.7 nm wavelength. This absorbance will affect the intensity of the radiation within the reactor; in specific design situations, the level of absorbance will affect the sizing of the system and possibly the configuration (spacing) of the lamps. The final product of these calculations is the average nominal intensity as a function of the UV absorbance coefficient.

## V. System Design and O&M Considerations for the UV Process

The design basis and the process elements which are key to the design of a UV system are:

- the hydraulic behavior of the unit,
- calculation of the intensity in the reactor, and
- generation of the appropriate water characterization data.

In this section are presented other peripheral topics which the designer (and operator) must consider. These factors will affect the operation and maintenance of the system, and the overall economics. Specifically, these factors include the elements which affect the reactor intensity (lamp output, lamp aging, and attenuation of intensity due to fouling of reactor surfaces), and methods for monitoring for lamp aging and unit fouling.

### Factors Affecting UV Intensity in a Reactor

**UV Lamp Output**: Output at any given time will be influenced by lamp temperature and by the voltage potential applied across the lamp. Additionally, output at the resonant frequency will always degrade with time of operation due to any number of "aging" factors. In the submerged systems, it is not practical under most design conditions to control the lamp temperature. In the non-contact systems, such as the tubular arrays, it is possible to maintain the lamps at their optimum wall temperature by controlling the temperature of the ambient air surrounding the lamps. This is being practiced currently in commercial applications. Heat given off by the lamp ballasts is circulated into the lamp reactor in cases where heat is required; otherwise fans vent the reactor with cooler outside air. These operations are controlled thermostatically.

**Voltage**: Radiance is a function of the arc current. This can be exploited by adjusting the voltage, in order to vary the output of the lamp. Decreasing the voltage will result in a decrease in the current. Such a control mechanism has been installed at full-scale facilities as an energy conservation measure. During periods of low UV demand, the lamps are "dimmed" by slowly turning the lamp supply voltage down. This results in a reduction in the power draw of the lamp. Generally, the lamp intensity can be reduced to levels no less than 50% before the lamp current becomes too low and the lamp will begin to flicker and eventually turn off.

**Lamp Aging**: A number of factors combine to effectively age a lamp and limit its useful life. These include failure of the electrodes, plating of the mercury to the interior lamp wall (blackening), and solarization of the lamp enclosure material (reducing its transmissibility). These all cause a steady deterioration in the lamp's output at the 253.7 nm wavelength, such that its output at the end of the lamp's life can be 40 to 60 percent of its nominal output.

The output of the lamp throughout its life is affected primarily by the extent of blackening and solarization of the glass tube; the actual life of the lamp is governed by the condition of the electrodes. The germicidal lamps are typically of the hot cathode type. These will deteriorate progressively with increasing number of starts. Thus, the lamp life expectancy generally is rated according to the number of times the lamp is started, or the burning cycle. The lamp life normally cited by most manufacturers is 7,500 hours, based on a burning cycle of eight hours. The average UV output at this point is estimated to be 70% of the lamp output at 100 hours (note that the nominal output of the low pressure mercury arc lamps represents its output after a 100 hour "burn-in" period).

## Monitoring the Lamp Intensity

The procedure for monitoring the lamp intensity is by comparison with that of a new lamp, but after the 100 hour burn-in time. The first step is to measure the intensity, at a fixed distance, of three to five new lamps which have been burned for about 100 hours. The average of the five then becomes the benchmark to determine the relative output of the lamps in use (percent of new lamp average). Each lamp should be tagged and given an I.D.

number; this allows direct monitoring of individual lamps and allows the operator to keep an appropriate mix of lamps in a system and to know when to discard a lamp.

The same procedure is used to monitor the transmittance of a quartz sleeve. In this case, a single lamp is used. First the intensity is measured with and without a new, clean quartz sleeve in place over the lamp. Similar measurements then are taken with the unit's quartz sleeves and compared to the transmittance of the new quartz. This can be done before and after the quartz is cleaned.

### vi. System Design Considerations for Effective Maintenance

An overriding concern in the proper maintenance of the UV reactor for effective performance is to keep all surfaces through which the radiation must pass as clean as possible. The effects of surface fouling on energy utilization efficiency are critical, and very often can be pointed to as the reason for non-performance of a particular system. Other concerns relate primarily to the accessibility to UV reactors and to keeping adequate records to control replacement cycles and maintenance schedules.

#### Reactor Maintenance

The most reliable method to determine if a reactor is becoming dirty and requires cleaning is by visual inspection. The unit should be drained and the surfaces observed for fouling. In open systems, this can be done rather conveniently and quickly. Reactors which are sealed vessels can be difficult. These designs should accommodate such visual inspections by incorporating large portholes or manways in the reactor shell.

Generally the surfaces of submerged quartz systems contacted by the water will become coated by inorganic scale, very much like boiler scale. This will be especially the case in areas where there is hard water. Additionally, the inside surface of the quartz and the outer surfaces of the Teflon tubes eventually will develop a grimy dust layer, primarily from airborne dirt and water vapor.

Fouling of the reactor's internal surfaces will be signaled by reduced performance efficiency, or by reductions in the intensity measured by in-line probes. While these may provide some signal of fouling, it is still necessary to be able to inspect the surfaces physically.

It is appropriate to completely overhaul the reactor, cleaning all interior surfaces, and determining the lamp outputs and quartz (or Teflon) transmittances. Each lamp is removed from the reactor and washed with a mild soap solution, rinsed, and swabbed with an alcohol (isopropyl) soaked rag (cheesecloth). Then the interior surfaces of the quartz sleeves are cleaned by the same procedure by using a gun-barrel type cleaning rod to swab the interior surfaces. At the same time, each lamp, which is tagged with an I.D. number, is measured for relative output. Those which are below a specified level are discarded and replaced with new lamps. These new lamps also are tagged with a number. In this manner, each lamp can be traced on the basis of operating time and output. A reactor lamp inventory then can be mixed and controlled to maintain a minimum average output level.

In similar fashion, the quartz should be monitored for transmittance. It may be cumbersome, however, to remove all the quartz from a system. It is recommended (U.S. EPA, 1986, p. 233), instead, that a representative fraction of the quartz sleeves be monitored; 10-15% of the quartz inventory would be sufficient. The same quartz should always be monitored; these would be considered as representative of all quartz in the system. If the tagged quartz begins to show marked deterioration due to aging and wear, it then may be appropriate to broaden the monitoring and to begin replacing the quartz sleeves. The replacement can be accomplished gradually. As with new lamps, eventually there will be a mix of old and new quartz in the system. There is little experience in determining the effective life of the quartz sleeves; certainly it will vary by site, but generally should be between four and seven years.

In Teflon systems, the lamps are removable on racks; they should be cleaned and monitored in the same manner as the quartz systems. The Teflon tubes should be cleaned on occasion; this can be done by swabbing the tubes with soapy water/alcohol. A non-abrasive material should be used. Each tube also should be monitored for transmittance, just as with the quartz sleeves. This may not be as straightforward, however, because of their limited accessibility and problems in getting direct measurements with a UV radiometer/detector.

## vii. **Costs for Disinfection With UV Radiation**

### Construction Costs

Table XXVIII summarizes costs developed in 1978 by Hansen et al. (1979). By 1982, these costs had increased about 15% (U.S. EPA, 1983) for the size ranges listed. Data presented are for single and multiple UV lamp disinfecting units ranging in water throughput capacity from 14,400 gal/day to 1,123,200 gal/day.

## TABLE XXVIII. CONSTRUCTION COSTS FOR ULTRAVIOLET LIGHT DISINFECTION

| Cost Category | Plant Capacity (gpd) 14,400 | 28,800 | 187,200 | 374,400 | 748,800 | 1,123,200 |
|---|---|---|---|---|---|---|
| Excavation and Sitework* | $ 60 | $ 60 | $ 60 | $ 60 | $ 80 | $ 110 |
| Manufactured Equipment | 800 | 1,125 | 4,485 | 8,685 | 17,365 | 26,050 |
| Concrete* | 250 | 250 | 250 | 250 | 280 | 300 |
| Labor* | 110 | 170 | 250 | 300 | 400 | 500 |
| Pipe and Valves* | 60 | 150 | 350 | 450 | 750 | 1,000 |
| Electrical and Instrumentation* | 430 | 430 | 430 | 430 | 480 | 480 |
| Housing* | 1,500 | 1,500 | 1,500 | 1,500 | 1,800 | 2,000 |
| SUBTOTAL | 3,210 | 3,885 | 7,225 | 11,675 | 21,155 | 30,440 |
| Miscellaneous and Contingency* | 470 | 560 | 1,010 | 1,580 | 2,830 | 4,060 |
| TOTAL | $3,680 | $4,445 | $8,335 | $13,255 | $24,085 | $34,500 |

* Data from Hansen et al. (1979).

All UV generating units are quite compact; for example, the 1,123,400 gal/day unit occupies an area of less than 24 $ft^2$. Costs listed in Table XXVIII include equipment costs of the UV units, and the related costs of piping, electrical equipment, equipment installation, and a building to house the equipment.

### Operating and Maintenance Costs

These are shown in Table XXIX (for 1979) for the same size plants as in Table XXVIII. Process energy is required for the mercury lamps operating inside of the UV generating units. Continuous 24-hr/day operation is assumed, with only occasional shutdown to clean cells and replace UV lamps which have become weakened by lengthy use. Building energy requirements are for heating, lighting, and ventilation.

Maintenance materials are related to the replacement cost of the UV lamps, which usually are replaced after operating continuously for about 2,000 hours (about eight months). Labor requirements are related to occasional cleaning of the quartz sleeves which surround the mercury vapor lamps, and periodic replacement of the weak UV bulbs.

It is noteworthy that replacement bulb costs at the smallest plant (14,400 gal/day) are only about 9% of the total O&M costs, whereas at the largest plant size (1,123,200 gal/day), replacement bulb costs are about 48% of the total O&M costs. This reflects the fact that the larger UV generating units contain a greater number of UV bulbs per unit volume of water treated.

## 2. Secondary Disinfectants

There are disinfectants which are added in small dosages to waters which have been treated with primary disinfectants. The purpose of secondary disinfectants is to maintain a small residual disinfectant in the distribution system.

In point of fact, there are three secondary disinfectants in prevalent use: chlorine, chlorine dioxide, and monochloramine. Considerations pertaining to chlorine as a secondary disinfectant are essentially the same as were discussed earlier for chlorine as a primary disinfectant.

## TABLE XXIX. OPERATION AND MAINTENANCE SUMMARY FOR ULTRAVIOLET LIGHT DISINFECTION

| Plant Flow Rate (gpm) | Energy (kWh/yr* | | | | Maintenance | Labor | | Total Cost |
|---|---|---|---|---|---|---|---|---|
| | Building | Process | Total | x $0.07/kWh = | Matl.*($/yr) | (hr/yr) | x $10/hr = | ($/yr) |
| 14,400 | 10,260 | 440 | 10,700 | $ 749 | $ 100 | 24 | $240 | $ 1,089 |
| 28,800 | 10,260 | 800 | 11,140 | 780 | 140 | 24 | 240 | 1,160 |
| 187,200 | 10,260 | 5,260 | 15,520 | 1,086 | 600 | 24 | 240 | 1,926 |
| 374,400 | 10,260 | 10,510 | 20,770 | 1,454 | 1,120 | 30 | 300 | 2,874 |
| 748,800 | 12,310 | 21,020 | 33,330 | 2,333 | 2,250 | 36 | 360 | 4,943 |
| 1,123,200 | 13,340 | 31,540 | 44,880 | 3,142 | 3,300 | 42 | 420 | 6,862 |

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* Data from Hansen et al. (1979).

Figure 9 plots estimated labor requirements for the operation and maintenance of UV systems (Scheible et al., 1985)

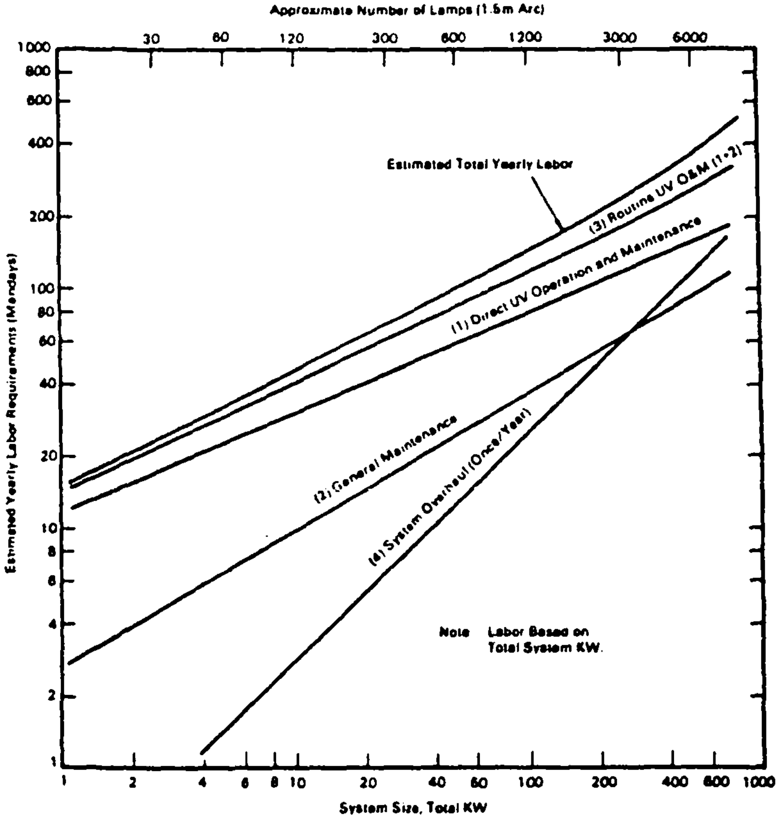

Figure 9. Estimate of labor requirements for the O&M of UV systems (Scheible et al., 1985).

## 2. Secondary Disinfectants

### a. Chlorine Dioxide

Chlorine dioxide ($ClO_2$) is an unstable, greenish-yellow gas, explosive in air in concentrations above 4%. Because of this instability, it is always generated in solution, on-site, and is used immediately without storage. As long as care is taken to keep chlorine dioxide in solution and storage of solutions is avoided, there will be no explosion hazards. Chlorine dioxide is readily soluble in water and is decomposed by sunlight.

The material is a more powerful oxidizing agent and a better biocide than is chlorine. In addition, when chlorine dioxide is prepared in the absence of excess free chlorine, its use will not produce trihalomethanes, or other chlorinated organic by-products of current public health concern. Additionally, chlorine dioxide has been used in pretreatment to oxidize phenolic compounds and to separate iron and manganese from organic complexes which are stable to chlorination.

Distribution system residuals of dissolved chlorine dioxide are longer-lasting than those of chlorine because there is no reaction with ammonia or formation of chlorinated organic materials. Additionally, chlorine dioxide is not known to impart tastes and odors to water, as does chlorine.

Recent health effects studies have shown (NAS, 1987) that chlorine dioxide produces hematological effects in both humans and laboratory animals. For these reasons, the U.S. EPA (1981) advises that the total concentration of chlorine dioxide and its decomposition products (chlorite and chlorate ions) be maintained below 1 mg/L.

Gaseous chlorine dioxide has a strong, disagreeable odor, similar to that of chlorine gas, and is toxic to humans when inhaled. It is detected by the human nose at concentrations between 1.4 and 1.7%. When present at 4.5% concentrations, it irritates the respiratory mucous membranes and may cause severe headaches. At concentrations below 6% in air, it may be compared with chlorine with respect to its toxicity (Masschelein, 1979). Eventual intoxications appear by local irritations of the nervous system, ocular and respiratory mucous membranes, without substantial resorption or systemic poisoning (Ehrlicher, 1964). There are no cumulative effects in cases of repeated exposure (Haller & Northgraves, 1955).

### i. Generation of Chlorine Dioxide

For drinking water treatment, chlorine dioxide is generated from solutions of sodium chlorite, $NaClO_2$. This material, purchased as a solid (80% $NaClO_2$) or most normally, as a 25% aqueous solution, is treated with aqueous solutions of chlorine or hypochlorous acid), and sometimes with a strong mineral acid such as sulfuric or hydrochloric acids.

Three processes used in water treatment plants for the generation of $ClO_2$ employ (a) gaseous chlorine, (b) sodium hypochlorite solution and mineral acid, and (c) mineral acid. Each process is summarized below.

### 1. Gaseous Chlorine

This is a two-step procedure, beginning with the formation of hypochlorous acid upon dissolution of gaseous chlorine into water:

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{H_2O} \text{------>} \underset{\substack{\text{hypochlorous}\\\text{acid}}}{HOCl} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{HCl}$$

These intermediate products then react with sodium chlorite to produce chlorine dioxide:

$$\underset{\substack{\text{hypochlorous}\\\text{acid}}}{HOCl} + \underset{\substack{\text{hydro-}\\\text{chloric}\\\text{acid}}}{HCl} + \underset{\substack{\text{sodium}\\\text{chlorite}}}{2NaClO_2} \text{---->} \underset{\substack{\text{chlorine}\\\text{dioxide}}}{2ClO_2} + \underset{\substack{\text{sodium}\\\text{chloride}}}{2NaCl} + \underset{\text{water}}{H_2O}$$

The end result of these reactions is summarized by the equation:

$$\underset{\text{chlorine}}{Cl_2} + \underset{\substack{\text{sodium}\\\text{chlorite}}}{2NaClO_2} \text{---->} \underset{\substack{\text{chlorine}\\\text{dioxide}}}{2ClO_2} + \underset{\substack{\text{sodium}\\\text{chloride}}}{2NaCl}$$

According to the stoichiometry of this equation, one mole of chlorine reacts with two moles of sodium chlorite to produce two moles of chlorine dioxide. In water supply practice, some molar excess of chlorine actually is employed so as to insure conversion of the maximum amount of chlorite ion to chlorine dioxide. Therefore, the recommended ratio of reactants is two moles of chlorine per mole of sodium chlorite. On a weight basis, 1.57 parts of chlorine gas are added per part of $NaClO_2$ (calculated on a 100% solids basis when solutions of sodium chlorite or 80% solids materials are employed).

Under these conditions of excess chlorine gas being added, the product $ClO_2$ solution also will contain an amount of hypochlorous acid/hypochlorite ions. These can react with THM precursor materials to produce THMs.

### 2. Sodium Hypochlorite and Mineral Acid

This also is a two-step process, in which sodium hypochlorite solution reacts with hydrochloric acid to form hypochlorous acid, which then reacts with sodium chlorite to form chlorine dioxide:

| $NaOCl$ | + | $HCl$ | ----> | $NaCl$ | + | $HOCl$ |
|---|---|---|---|---|---|---|
| sodium hypochlorite | | hydrochloric acid | | sodium chloride | | hypochlorous acid |

| $HOCl$ | + | $HCl$ | + | $2NaClO_2$ | -----> | $2ClO_2$ | + | $2NaCl$ | + | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| hypochlorous acid | | hydrochloric acid | | sodium chlorite | | chlorine dioxide | | sodium chloride | | water |

In this procedure, as in the gaseous chlorine and sodium chlorite procedure, excess chlorine is utilized to insure conversion of the maximum amount of chlorite ion to chlorine dioxide. The $ClO_2$ solution so produced also will be able to form some THMs because of the presence of excess hypochlorous acid.

### 3. Mineral Acid

This process involves mixing a solution of acid with a solution of sodium chlorite, and the reactions are depicted as follows:

| $5NaClO_2$ | + | $4HCl$ | ----> | $4ClO_2$ | + | $5NaCl$ | + | $2H_2O$ |
|---|---|---|---|---|---|---|---|---|
| sodium chlorite | | hydrochloric acid | | chlorine dioxide | | sodium chloride | | water |

When sulfuric acid is the strong mineral acid, the reactions can be depicted as follows:

| $10NaClO_2$ | + | $5H_2SO_4$ | ----> | $8ClO_2$ | + | $5Na_2SO_4$ | + | $4H_2O$ | + | $2HCl$ |
|---|---|---|---|---|---|---|---|---|---|---|
| sodium chlorite | | sulfuric acid | | chlorine dioxide | | sodium sulfate | | water | | hydrochloric acid |

The exact ratios of reactants will depend upon which mineral acid is employed for the production of chlorine dioxide.

When generated using mineral acid, excess chlorine is not required. Consequently, solutions of chlorine dioxide prepared in this manner do not contain free residual chlorine, thus no chlorinated organic by-products can be synthesized.

In all three cases, the appropriate aqueous solutions of reactants are metered into a chlorine dioxide reactor (a cylinder containing Raschig rings, glass beads, or hollow glass cylinders) where intimate mixing of the reacting solutions occurs (see Figures 10 and 11). The size of the reactor and the residence time of the reacting solutions are such that after a few seconds, the solution exiting the reactor displays a strongly yellow color of chlorine dioxide. This solution then is pumped directly into the water to be treated.

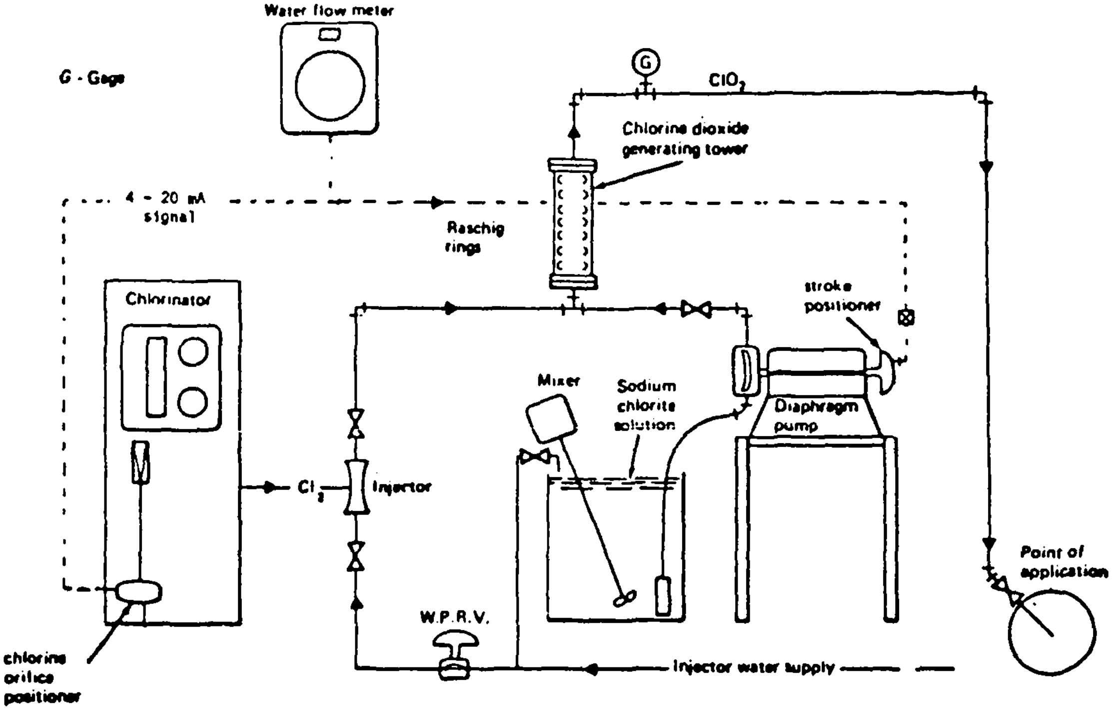

Figure 10. Schematic diagram of an automatic feed, automatic flow-proportional chlorine dioxide system: generation from chlorine and sodium chlorite (courtesy Capital Controls Co., Inc.).

In this manner, solutions of chlorine dioxide are generated as the material is required and used immediately, without storage. Appropriate metering and control instrumentation can be installed with the chlorine dioxide reactor so that the generation and addition of chlorine dioxide is paced by the flow rate of the water to be treated. As a result, the unit operates without the need for constant manual attention.

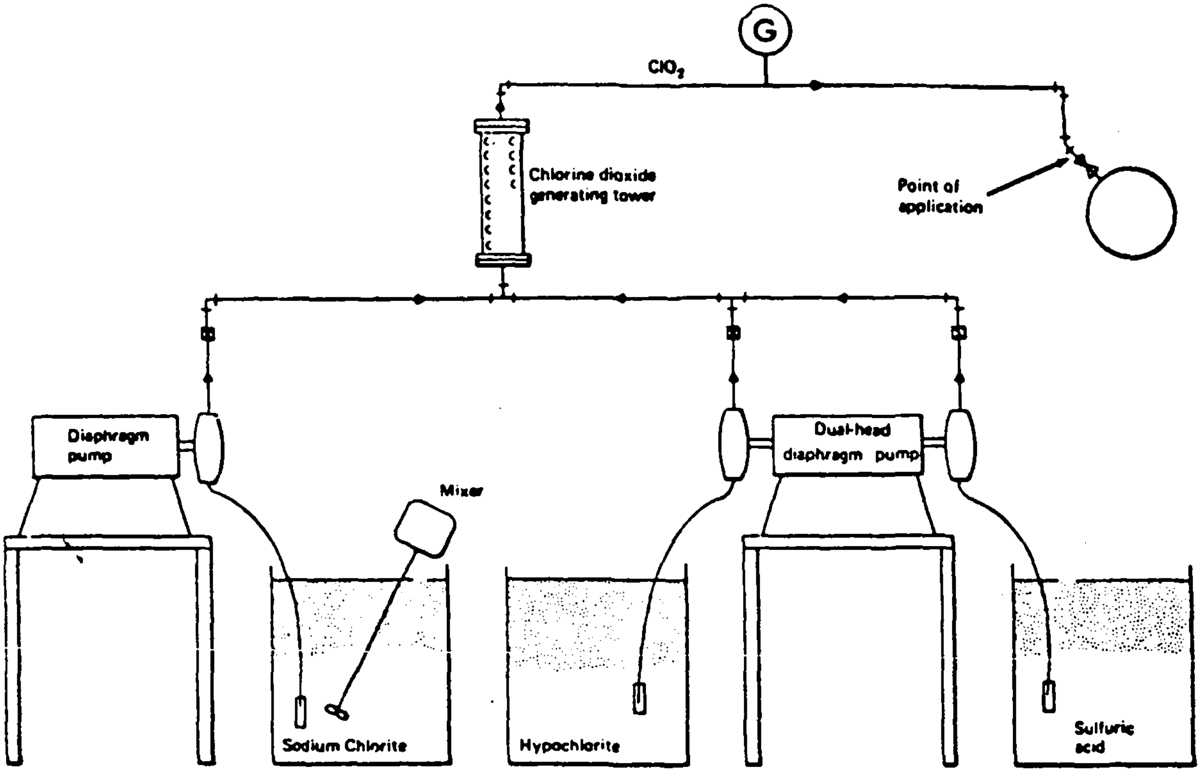

Figure 11. Manual feed equipment arrangement for generating chlorine dioxide from sodium hypochlorite solution and mineral acid (U.S. EPA, 1983).

### ii. Oxidation-Reduction Reactions of Chlorine Dioxide

At neutral pH (= 7) chlorine dioxide dissolves totally in water without hydrolysis reactions. On the other hand, when performing its function as a chemical oxidant or disinfectant in water, chlorine dioxide is chemically reduced. One of the reaction products is the chlorite ion, from which $ClO_2$ was formed initially:

$$\underset{\text{chlorine dioxide}}{ClO_2} \quad + \quad \underset{\text{reducing agent}}{e^-} \quad \text{---->} \quad \underset{\text{chlorite ion}}{(ClO_2)^-}$$

In strongly acid ($\leq$ 2) or strongly alkaline ($\geq$ 11) solutions, chlorine dioxide undergoes disproportionation (self oxidation and reduction):

$$2ClO_2 + H_2O \text{ ----> } (ClO_2)^- + (ClO_3)^- + 2H^+$$

| | | | | |
|---|---|---|---|---|
| chlorine dioxide | water | chlorite ion | chlorate ion | hydrogen ion |

These disproportionation reactions are accelerated by the presence of hypochlorous acid and hypochlorite ion. Therefore, when chlorine dioxide is generated in the presence of excess chlorine, chlorite and chlorate ions will be formed as well.

### iii. Establishing a Chlorine Dioxide Residual

Because the cost of chlorine dioxide is higher than that of chlorine, and because of the hematological effects upon both humans and laboratory animals, only small dosages of chlorine dioxide (maximum residuals of 1 mg/L total of $ClO_2$, chlorite, and chlorate ions) currently are recommended by EPA for drinking water treatment (U.S. EPA, 1981). However, a primary advantage of chlorine dioxide is that it does not react with ammonia or with THM precursors to produce THMs, as does chlorine. This means that if the water has been pretreated to remove most of the oxidant-demanding constituents (or does not contain them initially), the total $ClO_2$ dosage can be used to provide secondary disinfection at the recommended 1 mg/L maximum oxidant residual.

In laboratory studies, Werdehoff & Singer (1986) have shown that about 70% of the $ClO_2$ added is converted to chlorite ion. Therefore a chlorine dioxide dosage of 1.3 to 1.5 mg/L is the maximum practical dosage in order not to exceed the recommended 1 mg/L residual of total oxidant. This value has been confirmed by Lykins & Griese (1986) in pilot plant and full-scale plant studies at Evansville, IN (see Case History -- Evansville, IN, Section VIII.C.1).

### iv. Factors Affecting the Efficiency of Secondary Disinfection With Chlorine Dioxide

Chlorine dioxide is a more effective disinfectant than chlorine or hypochlorous acid. Because it does not react with water, ammonia, or most organic nitrogen compounds, it is not "wasted" in extraneous reactions of this type. It is less sensitive to changes in pH (except at very low and very high values), maintaining its disinfection capabilities over the pH range of 6 to 10.

On the other hand, because it is a more powerful oxidizing agent than chlorine or hypochlorous acid, chlorine dioxide can and will react with oxidizable impurities contained in a raw or treated water. Thus, it is important to ensure that oxidant-demanding components of the water have been removed to as low a level as is feasible, consistent with the costs involved, before chlorine dioxide is added.

## v. Chlorine Dioxide Systems Design

Table XXX is a partial listing of current suppliers of chlorine dioxide equipment. Several different types of generation equipment are available, which vary depending upon the supplier, but also upon the generation process chosen (gaseous chlorine versus sodium hypochlorite plus acid, versus acid plus sodium hypochlorite, for example). Pertinent aspects of each type of chlorine dioxide generation equipment will be discussed in this subsection.

TABLE XXX. PARTIAL LISTING OF CHLORINE DIOXIDE EQUIPMENT SUPPLIERS

| Name | Address |
|---|---|
| Capital Controls Co., Inc. | P.O. Box 211, Colmar, PA 18915 |
| CIFEC | 10 Avenue de la Porte Molitor, F-7500, Paris, France |
| Clow Corporation | 408 Auburn Ave., Pontiac, MI 48058 |
| Fischer & Porter Co. | County Line Road, Warminster, PA 18974 |
| Olin Water Services Co. | 9393 W. 110th St., Overland Park, KS 66210 |
| ProMinent Fluid Controls | 1005 Parkway View Drive, Pittsburgh, PA 15205 |
| Rio Linda Chemical Co., Inc. | 410 North Tenth Street, Sacramento, CA 95813 |
| Wallace & Tiernan Division Pennwalt Corp. | 25 Main St., Belleville, NJ 07109 |

## 1. Gaseous Chlorine Plus Hypochlorite Solution

All three of the chlorine dioxide generation procedures described earlier are in general use in the United States at this time for application in small water treatment facilities. The most commonly used procedure involves addition of gaseous chlorine to sodium chlorite solutions. A schematic diagram of chlorine/-sodium chlorite equipment is shown in Figure 10.

The gaseous chlorine procedure is particularly applicable when a gaseous chlorination system already exists at the treatment plant. The reaction by which chlorine dioxide is generated is as follows:

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{sodium chlorite}}{2NaClO_2} \longrightarrow \underset{\text{chlorine dioxide}}{2ClO_2} + \underset{\text{sodium chloride}}{2NaCl}$$

This equation indicates that 71 lbs (26.48 kg) of chlorine mixed with a solution containing 181 lbs (67.5 kg) of 100% $NaClO_2$ will produce 135 lbs (50.36 kg) of chlorine dioxide. However, the ratio of reagents recommended by most suppliers of chlorine dioxide generating equipment is 1:1 by weight. This means that more than double the stoichiometric amount of chlorine required by the above equation is utilized. This excess of chlorine over that required results in a faster reaction rate and insures a more complete conversion of chlorite ion to $ClO_2$.

However, because a large excess of chlorine is employed, solutions of chlorine dioxide prepared by this technique also will contain some free available chlorine, mostly as hypochlorous acid. This amount of free chlorine will produce some quantity of trihalomethanes and other halogenated products.

## 2. Hypochlorite, Chlorite, and Acid

The production of chlorine dioxide using sodium hypochlorite solution with sodium chlorite and acid is illustrated in Figure 11, and is well suited to most small water systems. Dosages of each chemical can be derived from the equations given earlier.

In this system, all three reactants are in solution. Utilization of acid increases the conversion of chlorite ion to chlorine dioxide. Solution feed pumps of equal capacities can be used by adjusting the solution strength of each of the reactants. Thus, the chlorine dioxide production and addition rates can be paced by the flow rate of the water being treated and/or by its secondary disinfectant demand.

Sodium chlorite is available in 55-gal (208.33 L) drums, either as a solid (80% active $NaClO_2$) or as a solution containing 30% $NaClO_2$ (33% solids). If not used directly from the drum, sodium chlorite solution is stored in poly(vinyl chloride) (PVC) or fiberglass tanks and transferred by means of PVC, rubber, or Tygon tubing systems. Diaphragm pumps incorporating PVC as the material in contact with the solutions are used for pumping sodium chlorite solutions. Provision must be made for immediate washdown of any spills of the chemical. This precaution is generic to **all** chlorine dioxide generating systems.

## 3. The CIFEC system for Generating Chlorine Dioxide

A schematic diagram of this system, developed in France, but in use at several U.S. water treatment plants, is illustrated schematically in Figure 12. The system produces $ClO_2$ from gaseous chlorine, in high yield, and containing little excess free chlorine.

Gaseous chlorine is passed into water which is circulated continuously in what is referred to as an "enrichment loop". Under these conditions, dissolved chlorine (hypochlorous acid) concentrations become higher than can be achieved in a single pass. As a result, the pH of the hypochlorous acid solution is lowered to below 4. This solution then is pumped into the $ClO_2$ reactor along with a solution of sodium chlorite. As long as the pH of the hypochlorous acid solution is below 4.0, conversion of chlorite ion to chlorine dioxide is significantly higher than the single pass method employing elemental chlorine gas. Therefore, chlorine dioxide is produced which is free of significant quantities of free chlorine.

## 4. Rio Linda Chlorine Dioxide Generator

Figure 13 shows a schematic diagram of a newer acid/chlorite chlorine dioxide generator marketed by Rio Linda Chemical Co., Inc. Chlorine dioxide is generated by addition of dilute hydrochloric acid to sodium chlorite solution. The novel principle of this generator is the mixing of acid with concentrated sodium chlorite solution just before the two solutions reach the reactor. The two solutions are brought together in an eductor by means of a vacuum created by water flow through the eductor. Such a system eliminates a pump and allows the system to occupy a smaller space.

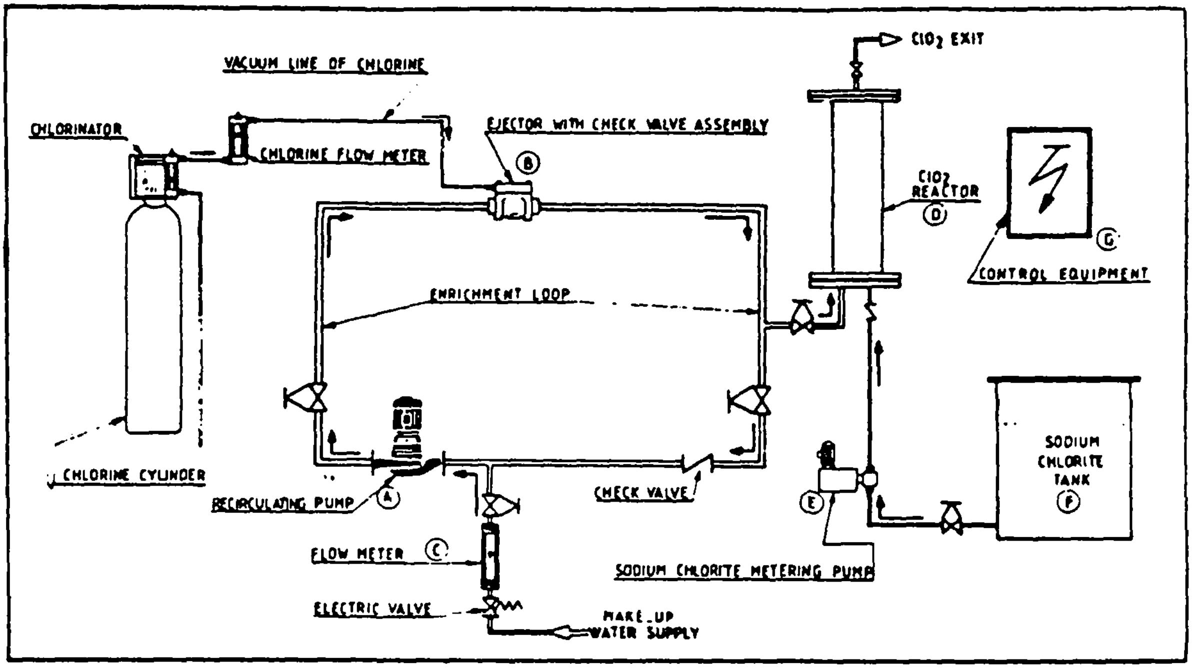

Figure 12. Schematic of the CIFEC chlorine dioxide generating system.

### vi. **Miscellaneous Comments**

Because several types of chlorine dioxide equipment are available, as well as three processes for its production, it is considered inappropriate to attempt to provide detailed instructions in this document for the preparation of chemical solutions and feed rates. However, the small water utility choosing to install chlorine dioxide generating equipment can have confidence that each equipment vendor will provide detailed recipes for preparing and metering the appropriate solutions to his chlorine dioxide reactor so as to produce an aqueous solution of chlorine dioxide of known and constant concentration for addition to the plant process water.

A final point to be noted is that the currently recommended maximum concentration of total oxidants (chlorine dioxide, chlorite and chlorate ions) of 1 mg/L means that a water utility processing 0.5 mgd (1,893 $m^3$/day) and dosing 1 mg/L of chlorine dioxide will require a maximum $ClO_2$ production rate of only 4 lbs (1.82 kg)/day. Smaller systems will require even less $ClO_2$. At such low dosage levels, two of the three vendors of chlorine dioxide contacted recommend that their units be operated intermittently, collecting $ClO_2$ solution in an enclosed holding tank for metering into the water being processed. This is because at the low flow rates of reactant solutions, mixing is less efficient in the chlorine dioxide reactor. Consequently, conversion of chlorite ion to chlorine dioxide is less efficient.

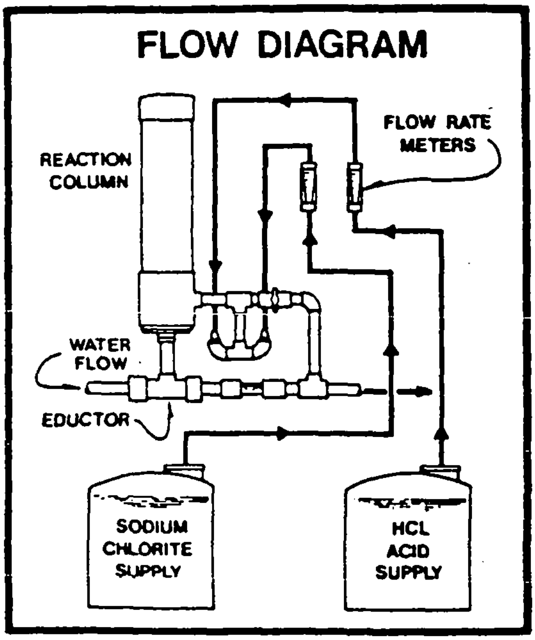

Figure 13. Schematic of the Rio Linda Chemical Co. acid/-$NaClO_2$ chlorine dioxide generator.

### vii. Costs of Chlorine Dioxide Generating Systems

Hansen et al. (1979) summarized costs for the generation of chlorine dioxide from equal parts of 2.4% sodium chlorite solution, 25% sulfuric acid solution and 1% sodium hypochlorite solution. Suppliers contacted in 1982 had changed the design of their generation systems for small water supply systems to use 33% hydrochloric acid rather than 25% sulfuric acid.

Equipment costs estimated by Hansen et al. (1979) assumed the use of a dual head diaphragm pump for simultaneous addition of hypochlorite and acid solutions, and a single head pump for the addition of sodium chlorite solution. Detention time in the chlorine dioxide reactor is estimated at 12 seconds, and the generating equipment costs are assumed to be constant up to 50 lbs/day of chlorine dioxide.

At a maximum chlorine dioxide dosage rate of 1 mg/L, a 1 mgd water treatment plant would dose 8 lbs/day. At the same dosage level, a 2,500 gal/day water facility would require only 0.2 lb/day of chlorine dioxide.

## Equipment Costs

Quotes were obtained (U.S. EPA, 1983) from three suppliers of chlorine dioxide generation equipment sized so as to prepare $ClO_2$ at the rate of 8 lbs/day (for a 1 mgd water treatment plant). These are shown in Table XXXI. Supplier A's recirculating loop system (CIFEC) is the highest in equipment price; their lowest cost unit was priced at $34,000 in 1982. This unit operates with a special recirculating pump designed to handle hypochlorous acid below pH 4; plus a sodium chlorite solution pump and all necessary instrumentation to allow automatic operation, with shutdown provisions in the event of cessation of water flow.

The next lowest in price is the system from Supplier B, which generates chlorine dioxide from 33% hydrochloric acid, 12% sodium hypochlorite, and 25% sodium chlorite solution. This unit cost $25,000 (installed) in 1982, and includes three solution pumps, water flow rate detector, and switches to shut down the unit if the water flow stops. This unit is wall mounted and requires 3.5 x 4 ft of wall space, plus floor space for drums of the three chemical solutions used to feed the generator. For volumes of $ClO_2$ sufficient to treat flows in communities of 5,000 and 2,500 population, this unit is said to be capable of continuous operation, with no loss in efficiency of conversion of chlorite ion to chlorine dioxide. However, to supply the needs of systems serving as few as 25 persons, the unit would have to be operated intermittently, with $ClO_2$ solution being stored in a holding tank for later metering into the water.

Supplier C provides two types of chlorine dioxide generators for small water supply systems. One uses acid/sodium chlorite, the other uses chlorine gas and sodium chlorite. These units cost $3,600 in 1982, if wall-mounted, and $4,320 for a floor-mounted cabinet. The single size unit offered by this supplier is designed to generate up to 140 lbs/day. In order to produce 8 lbs/day or less, a small water utility would have to install a holding tank and operate the generator intermittently.

TABLE XXXI. 1982 VENDOR QUOTES -- CHLORINE DIOXIDE GENERATORS

| Vendor | $ClO_2$ production capacity (lbs/day) | space required* | Reactants | Unit Cost |
|---|---|---|---|---|
| Recirculating loop Supplier A (French) | 1-10 | 2x3x6 ft | $Cl_2$ gas + $NaClO_2$ solution | $34,000 (1 rate, adjust manually) |
| | | | | $38,000 (2 rates (adjust automatically) |
| | (prices delivered to New York) | | | $41,700 (3 rates (adjust automatically) |
| Supplier B | 4 | 3.5x4x1.5 ft (wall-mounted | HCl, NaOCl<br>$NaClO_2$ solutions | $25,000 (installed) |
| Supplier C | 14-140 | 4x3x1.5 ft | $Cl_2$ gas + $NaClO_2$ soln. | $ 4,320** (floor mount) |
| | | 37.5x27x 6.5 in. | same | $ 3,600** (wall mount) |
| Supplier C | 14-140 | 4x3x1.5 ft | HCl + $NaClO_2$ soln. | $ 4,320 (floor mount) |
| | | 37.5x27x 6.5 in. | same | $ 3,600 (wall mount) |

* all units require additional space for solution tank(s).

** this unit requires a chlorinator for operation, which is not included in price estimates.

The chlorine gas/sodium chlorite generator of Supplier C requires a gas chlorinator to feed chlorine gas. Therefore, in new plants considering use of this type of equipment, the cost of a chlorinator must be added to the cost of the chlorine dioxide generator. In existing plants currently using gas chlorination, the chlorinator already is in place and would not represent additional equipment cost.

Because equipment quotes for generating chlorine dioxide vary so widely, water treatment personnel are advised not to try applying past equipment cost estimates. Technology for generating and applying chlorine dioxide is changing rapidly (as opposed to technologies for addition of gaseous or aqueous chlorine), and new suppliers enter the market from time to time. It is more advantageous to seek quotations from the various suppliers as to the various methods for generating $ClO_2$. Select the methods most appropriate to the specific water treatment plant, then determine what piping and wiring will be needed to install the equipment selected.

## Operation and Maintenance Costs

Hansen et al. (1979) concluded that, in general, O&M costs for generating $ClO_2$ are independent of the quantities generated. Process energy requirements, which are for metering pumps and mixer for preparing chlorite solution from solid sodium chlorite, are estimated at 1,240 kWh/yr. Energy requirements for 40 $ft^2$ of building space to house the equipment would be 4,100 kWh/yr, resulting in total energy requirements of 5,340 kWh/yr. Maintenance material requirements would be for minor equipment repair only, amounting to about $100/yr. Labor is required for preparation of solutions and periodic maintenance of the equipment. Annual labor requirements are estimated to be 1 h/day, or 365 h/yr.

Annual O&M costs of $4,124/yr (based on $0.07/kWh power cost and $10.00/h labor cost) are summarized in Table XXXII.

## Chemical Costs

At a production rate of only 8 lbs/day (maximum for a 1 mgd water treatment plant), chemical costs are not as significant as pumping costs. Nevertheless, 1982 chemical costs were as follows:

| | |
|---|---|
| gaseous chlorine | $0.47/lb |
| sodium chlorite | 1.55-1.65/lb |
| HCl | 0.10/lb |
| NaOCl | 0.93/gal (15% solution) |

Prices for chlorine and sodium chlorite in 1987 are about 30% lower.

A chlorine dioxide production rate of 8 lbs/day equates to 2,920 lbs/yr. If the chemicals cost for $ClO_2$ is arbitrarily assumed to be $1/lb, a 1 mgd water treatment plant can expect to pay about $2,920 in addition to the annual O&M costs. On the same basis, chemical costs at a 2,500 gal/day plant would be $2,920/400 = $7.30/yr for producing chlorine dioxide at $1.00/lb.

TABLE XXXII. OPERATION AND MAINTENANCE SUMMARY FOR CHLORINE DIOXIDE GENERATING AND FEED SYSTEMS

| Item | Requirements* | Cost |
|---|---|---|
| ELECTRICAL ENERGY | | |
| Process | 1,240 kWh/yr x \$0.07 = | \$ 86.8 |
| Building | 4,100 kWh/yr x \$0.07 = | \$ 287.0 |
| TOTAL | 5,340 kWh/yr x \$0.07 = | \$ 373.8 |
| MAINTENANCE MATERIAL | | \$ 100/yr |
| LABOR | 365 h/yr x \$10.00 = | \$3,650 |
| Total Annual O&M Cost | | \$4,124 |

* based on estimates of Hansen et al., 1979

### b. Chloramination

Chloramines are formed when water containing ammonia is chlorinated, or when ammonia is added to water containing chlorine (hypochlorite or hypochlorous acid). This is accomplished currently by adding gaseous ammonia (purchased as the anhydrous liquid, $NH_3$, in 150 lb cylinders) directly to the water, or by adding a solution of ammonium sulfate, $(NH_4)_2SO_4$ (purchased in 100 lb bags, 98% pure; 25% available $NH_3$).

### i. Chemistry of Chloramination

Three chloramine compounds can be produced, depending on the ratios of chlorine and ammonia which are utilized:

$$\underset{\text{ammonia}}{NH_3} + \underset{\text{hypochlorous}}{HOCl} \dashrightarrow \underset{\text{water}}{H_2O} + \underset{\text{monochloramine}}{NH_2Cl}$$

$$NH_2Cl + HOCl \dashrightarrow H_2O + \underset{\text{dichloramine}}{NHCl_2}$$

$$NHCl_2 + HOCl \dashrightarrow H_2O + \underset{\text{nitrogen trichloride}}{NCl_3}$$

The distribution of the chemical species of chloramines is a function of pH and of the amount of chlorine added. For example, in the pH range of 7 to 8 and a chlorine to ammonia weight ratio of 3:1, monochloramine is the principal product. At higher chlorine to ammonia ratios or at lower pH values (5 to 7), some dichloramine will be formed. If the pH drops below 5, some nitrogen trichloride (often erroneously called "trichloramine") may be formed. This compound should be avoided because it imparts undesirable taste and odor to the water.

Figure 14 (National Academy of Sciences, 1980) shows the relative percentages of monochloramine and dichloramine produced as the pH changes, for different weight ratios of chlorine to ammonia. At a pH value of about 5.7, approximately equal amounts of mono- and dichloramines are present in solution.

Care also should be taken not to exceed chlorine to ammonia ratios of 5:1. This is the ratio existing at the peak of the breakpoint curve, above which all of the ammonia will have been removed, chloramines will be absent, and free residual chlorine will be present.

### ii. Establishing a Chloramine Residual

Generation of chloramines is conducted on-site, in solution, as required, simply by adding the appropriate amount of chlorine to waters already containing ammonia, or by adding ammonia to waters already containing chlorine, then allowing a short holding time to be certain that the chemicals have had time to react with each other to form chloramines. Usually, chloramine-forming reactions are at least 99% complete within several minutes.

However, the National Academy of Sciences (NAS, 1987) has recommended rejection of the first approach (adding chlorine to ammonia-containing water). Furthermore, when using the second approach, the NAS recommends addition of sufficient chlorine to produce a slight residual of free chlorine above that required to oxidize nitrogen (particularly the organic nitrogen compounds), followed by addition of ammonia to form monochloramine and limit THM (and TOX) formation.

### iii. Chloramination System Design

Ammonia is available as the anhydrous gas ($NH_3$), as a 29% water solution (aqua ammonia), or in powdered form as ammonium sulfate $(NH_4)_2SO_4$. Gaseous ammonia is supplied in 150-lb (68.1 kg) cylinders, similar to gaseous chlorine. Aqua ammonia is supplied in 55 gallon (208.33 L) drums. Ammonium sulfate is available in 100-lb (45.4 kg) bags (98% pure, 25% available ammonia).

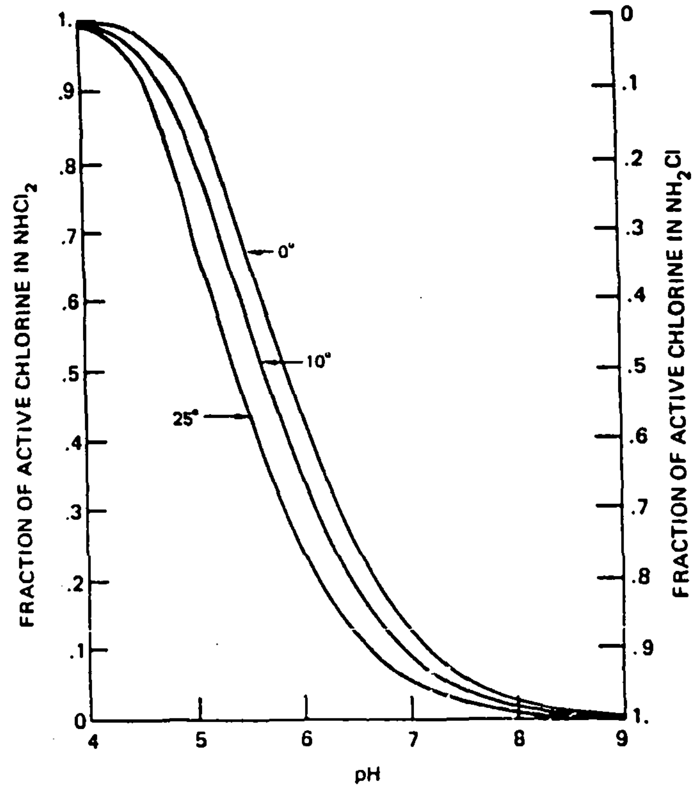

Figure 14. Proportions of mono- and dichloramines in water with equimolar concentrations of chlorine and ammonia (NAS, 1980).

Gaseous ammonia normally is added to the treated water using systems and equipment similar to those used for gaseous chlorine. Aqua ammonia and ammonium sulfate solutions are handled using systems and equipment similar to those for sodium hypochlorite and calcium hypochlorite solutions, respectively. Aqua ammonia is basic, but is non-corrosive.

Sizing of the treatment facility must take into consideration the intended 3:1 chlorine/ammonia ratio.

A 25% to 30% solution of ammonium sulfate in water is prepared in a plastic or fiberglass container and added to the water by means of a chemical metering pump. Solutions of ammonium sulfate are stable, but are acidic, and therefore can be corrosive to some metals. Materials which will withstand dilute sulfuric acid also will easily resist any possible corrosion effects of dilute ammonium sulfate solutions.

### iv. Costs for Chloramination

Generation of chloramines requires the same equipment for chlorination (gaseous or aqueous hypochlorination) plus equipment for the addition of ammonia (gaseous or aqueous). Costs for chlorination equipment and for its operation and maintenance have been presented earlier. In this section, costs for addition of ammonia are presented.

During January 1983, costs for liquid ammonia were $0.40/lb (in 150-lb cylinders), $0.70/lb of contained ammonia in 28% solution (purchased in 55 gal drums), and $0.51/lb for solid ammonium sulfate (purchased in 100 lb bags), in the Washington, DC-Baltimore area.

Cost calculations given below are based on the following reaction of chlorine gas and ammonia to produce monochloramine:

$$NH_3 + Cl_2 \text{ ----> } ClNH_2 + HCl$$

In addition, the calculations assume a dosage of 2.5 mg/L of chloramine as the secondary disinfectant. This is the maximum level currently recommended by the EPA to be present in distribution systems. It is further assumed that the chloramines will be produced by adding ammonia to water already containing free available chlorine. Finally, cost calculations are based upon chlorine added as the gas. By using previously described calculations involving solutions of sodium hypochlorite or of calcium hypochlorite, the amounts of these chlorinating agents required to produce monochloramine can be calculated readily.

### 1. Costs for Monochloramine From Anhydrous Ammonia + Chlorine Gas

A 2,500 gal/day water treatment plant will require 0.05 lb/day (23.66 g) of monochloramine at a dosage of 2.5 mg/L. According to the stoichiometry of the above equation for the generation of monochloramine from ammonia and chlorine, each gram-molecular weight (weight of one mole of compound expressed in grams) of monochloramine will require 1 gram-molecular weight each of ammonia and chlorine. Thus:

$$17 \text{ g } NH_3 + 71 \text{ g } Cl_2 \text{ ----> } 51.5 \text{ g } ClNH_2 + 36.5 \text{ g } HCl$$

Since 23.66 g of monochloramine are required each day, the corresponding amounts of ammonia and chlorine required are:

<u>Ammonia</u>: (23.66/51.5) x 17 = 7.81 g/day

<u>Chlorine</u>: (23.66/51.5) x 71 = 32.61 g/day

Dividing the grams of each reactant by 454 (the number of grams per pound), gives a daily requirement of 0.017 lb of ammonia and 0.0715 lb of chlorine. Multiplying each of these figures by 365 days yields the annual number of pounds of ammonia and chlorine required. Finally, annual costs for each are calculated by multiplying the annual requirements by the current costs:

<u>Ammonia</u>: 0.017 lb/day x 365 = 6.205 lb/yr x \$0.40/lb = <u>\$2.48</u>/yr

<u>Chlorine</u>: 0.0715 lb/day x 365 = 26.10 lb/yr x \$0.47/lb = <u>\$12.27</u>

The sum of these two numbers (\$2.48 + \$12.27) = \$14.75, total annual costs for the 2,500 gal/day facility.

A 1 mgd facility will require 400 times the amounts of chemicals at the same 2.5 mg/L dosage, therefore:

\$14.75 x 400 = <u>\$5,898</u>, annual chemical costs.

2. <u>Costs for Monochloramine From Aqua Ammonia + Chlorine Gas</u>

From the preceding calculations, the 2,500 gal/day facility will require 6.205 lbs/yr of anhydrous (gaseous) ammonia. If the source of ammonia is 28% aqueous ammonia, the calculation of costs is as follows:

1 gal of 28% ammonia weighs 8.34 lbs and contains 8.34 x 0.28 = 2.34 lbs of ammonia.

6.205 lbs/yr ammonia requires 6.205/2.34 = 2.55 gal/yr of aqua ammonia.

At \$0.70/lb of ammonia contained in aqua ammonia, the annual cost of aqua ammonia is:

6.205 lbs x \$0.70/lb = \$4.35/yr.

The annual cost of gaseous chlorine is \$12.27/yr, therefore the total annual chemical costs are:

\$4.35 + \$12.27 = <u>\$16.62</u>/yr.

The 1 mgd water treatment plant will require 400 times the amounts of chemicals:

> $16.62/yr at the 2,500 gal/day plant x 400 = <u>$6,648</u>/yr at the 1 mgd plant.

### 3. <u>Costs for Monochloramine From Ammonium Sulfate + Chlorine Gas</u>

One pound of ammonium sulfate contains 0.2576 lb (28.76%) of available ammonia. The 2,500 gal/day plant using solid ammonium sulfate will require 6.205 lbs of anhydrous ammonia annually. To obtain this amount of available ammonia requires 6.205/0.2576 = 24.09 lbs/yr of ammonium sulfate. At $0.51/lb, the 2,500 gal/day plant will require:

> 24.09 lbs/yr x $0.51/lb = $12.29/yr + $12.27 for chlorine
> = $24.55/yr.

The 1 mgd facility will require 400 times as much chemicals, or:

> $24.55 x 400 = $9,820/yr.

# VIII. CASE EXAMPLES OF EMERGING TECHNOLOGIES

Several examples of the use of disinfectants other than chlorine are presented in this section. The objectives of the different approaches described are (1) to attain the desired degree of disinfection and (2) to minimize the formation of disinfection by-products. Some of the examples illustrate changes in disinfection/oxidation techniques to cope with problems in addition to disinfection by-products, e.g., taste and odor, color, algae, etc.

Case histories presented include examples of the use of ozone as a primary disinfectant for controlling Giardia lamblia cysts at one plant and as a preoxidant for lowering THM levels at another.

Another case history involves a surface water treatment plant which has installed UV for primary disinfection, followed by chlorination for secondary disinfection.

Other examples involve uses of chlorine dioxide for preoxidation and for post-disinfection, of chloramines to lower THM concentration, and of combinations of chlorine dioxide and chloramine to lower THM concentrations.

## A. OZONE CASE HISTORIES

### 1. North Andover, Massachusetts[1]

### Ozone Disinfection for Giardia lamblia

#### a. The Problem

During early 1986, 18 cases of Giardiasis were reported in the North Andover area. On May 1, residents there were instructed to boil their tap water for at least five minutes while public health officials sought to locate and correct the problem.

North Andover's water supply, Lake Cochichewick, was found to contain Giardia cysts in samples taken in April 1986. Local officials confirmed that the lake's watershed has a large muskrat population, and there has been concern that residential septic

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[1] The author is indebted to Messrs. Ross Hymen and Paul Anderson of the Massachusetts Department of Environmental Quality Engineering, Mr. Tom Boshar of Lally Associates, the consultants on this project, and to Bill Nezgod and Dr. Carl Nebel, of PCI Ozone Corporation, suppliers of the ozonation equipment, for providing information on this case history.

systems were not working well enough to prevent harmful effects in the lake.

At the time of the Giardiasis outbreak, treatment of North Andover water supply involved pumping of Lake Cochichewick water through two pumping stations into the distribution system without filtration, but with chlorination. High humic concentrations have resulted, over the years, in the formation of a significant scale in the pipes, containing a significant amount of biofilm as well.

Heavier chlorination overcame the Giardia problem, but caused a second water quality problem. Descaling in the old distribution system piping released coliform organisms into the water supply. The presence of coliforms caused the State DEQE to continue the "boil water" notice until the coliform organisms could be shown to be absent.

In addition, THM levels of the chlorinated water rose to above 200 ug/L. Also, residents began complaining about high chlorine concentrations. Ozonation was investigated and was found to have promise.

Total coliforms in the Lake Cochichewick raw water normally are between 50 and 500 per 100 mL, and raw water turbidities normally are between 1 and 2 NTU.

### b. The Interim Solution

In early October, 1986, two ozonation systems (ozone generators, contactors, and exhaust gas destruction) began operating at the two Lake Cochichewick pumping stations in response to the emergency situation. Two discrete ozonation systems, one capable of generating 50 lbs/day of ozone, the second capable of generating 150 lbs/day, were rented from the ozonation equipment supplier for a period of time. Later, when the efficacy of the ozonation was proven, the town purchased and installed two 150-lb/day ozonation systems in the two pumping stations.

Therefore, as an interim solution, the lake water is being treated with ozone at the two pumping stations. Each pumping station pumps 2.5 to 3 mgd. At four points in the distribution system, chlorine is added to provide a residual disinfectant.

The state DEQE provided emergency funding of $2.5 million, which provided for the ozonation systems, for connecting pipelines to the three neighboring communities, for relining pipes with cement, and replacing water mains.

Rental fees for the two ozonation systems totaled approximately $90,000. The two 150-lb/day ozonation systems were purchased for

$325,000. This fee included the air preparation system, ozone generation, diffuser contactors, and ozone destruction equipment, plus the appropriate instrumentation, including a monitor for measuring residual ozone at the outlet of the contact chamber. These two ozonation systems were installed as a stop-gap measure to control Giardia cysts until a proposed $10.5 million water 12-mgd plant is designed and constructed, and which will provide complete treatment, including filtration and ozonation (in mid-1989).

The two ozone contacting chambers (each 10 ft wide x 20 ft long, with a 16-ft water depth) are designed with baffles, to provide each contactor with five complete mix ports, with ozone being applied equally in each section. Thus, there is plug flow throughout the ozone contactors. Applied ozone dosages are 5 mg/L.

At the outlet of each contact chamber, the concentration of ozone lies between 0.9 and 1.0 mg/L. System designers assume that the average ozone concentration in each contactor is 0.5 mg/L. Total residence time of water in the ozone contact chamber is 10 minutes at full pumping rate (summer time). During winter, with lower water demand, pumping rates are reduced by 50%, thereby doubling the residence time in the contactors to 20 minutes.

Water temperatures of the lake vary from about 5°C in winter to just under 20°C during summer. Therefore, the appropriate CT values listed in Table IIA for 99.9% inactivation of Giardia lamblia range from 3 to 1.5. Assuming the average dissolved ozone concentration of 0.5 mg/L carried through the 10 minute contact period, the summertime CT value attained is 5.

During winter, when the contactor residence time is 20 minutes, the CT value attained is 10. Both of these CT values are well in excess of the 3 to 1.5 required to guarantee 99.9% inactivation of Giardia lamblia and 99.99% inactivation of viruses.

No filtration is provided during the current interim period. Instead, the community is placing total reliance on ozone for primary disinfection plus secondary chlorination.

### c. The Results

After approximately 90-days of ozone treatment, the State DEQE unconditionally lifted the boil water order, which had been in effect for nine months. Not only are Giardia cysts absent from the North Andover water supply, but also coliform organisms.

In addition, several additional benefits have been obtained as a result of installing ozonation. Prior to ozonation being installed, THM values were in the range of 8 to 120 ug/L. Since ozonation has been installed, THM values now are in the range of 1.1 to 2 ug/L. In addition, the color of the treated water has improved significantly (65% to 95% lower). Finally, taste and odor levels in the finished waters are greatly improved.

### d. For The Future

As indicated earlier, a new 12-mgd conventional treatment plant, including ozonation and granular activated carbon adsorption, has been designed. Preozonation will be applied before the rapid mix. After dual media filtration, GAC adsorption is incorporated, followed by post-chlorination for residual. In addition to providing an adsorption capability, the GAC step also will allow biological decomposition of the easily biodegraded organic fractions of the water present at that treatment point.

Bids were let for this plant in the summer of 1987; the plant is scheduled to be on-line by mid-1989.

### e. Note - Sturgeon Bay, WI

A second plant is installing ozone specifically for controlling Giardia lamblia contamination in Sturgeon Bay, WI. This is a groundwater plant, without filtration, located on a Lake Erie shore, which has been shown to contain Giardia cysts. Water flow at this treatment plant is 100,000 gal/day. Water temperature is about 10°C the year round.

Two 4-minute residence time ozone contactors are being installed. After contacting, the ozone-containing water will be stored in a filling well. Thus, the total ozone contact time is estimated to be 10 minutes. Dissolved ozone concentrations at the outlet of both contactors will be adjusted to 1 mg/L.

Thus the CT value in the second ozone contact chamber will be 4 (4 minutes times 1 mg/L), plus a conservatively estimated 2 in the first chamber (0.5 mg/L times 4 minutes), plus an additional 1 in the filling well, during ozone decay from 1 mg/L. The total CT value designed is 7. Table IIA requires a CT value of only 2.5 for 10°C.

The retrofitted ozonation system is expected to be operating in October, 1987.

## 2. Kennewick, Washington (Cryer, 1986) - Preozonation For THM Control

### a. The Problem

Prior to 1977, the City of Kennewick had been drawing essentially all of its municipal water supply from a system of five Ranney Collectors located along the Columbia River, followed by chlorination. When initially installed, these were capable of producing approximately 20 mgd; however, their output had deteriorated to about 15 mgd by 1977. By 1978, the maximum daily system demand essentially had reached the capacity of the Ranney system. It was determined that direct utilization of the Columbia River would be the only reliable source of supply for long term development.

A consequence of this decision was the need to provide considerably more treatment to achieve the same or better finished water quality. Thus a pilot plant study was undertaken to test alternative water treatment processing steps. This study included the use of preozonation and of post-filtration GAC adsorption, in addition to conventional and direct filtration procedures.

Average values of the water quality parameters of the raw Columbia River are:

| | | |
|---|---|---|
| TTHM | 1 | ug/L |
| TTHMFP* | 136 | ug/L |
| TOC | 2.4 | mg/L |
| No. Particles | 11,650 | /mL |
| Particle Volume | 160,700 | nanoL/L |
| Turbidity | 1.7 | NTU |

* Chlorine contact time: 1 week

### b. Pilot Plant Study Results

Both the preozonation and coagulation/filtration steps provided approximately 30% reduction in levels of TTHM formation potential and 10% reduction in TOC levels. The combined processes gave approximately 60% reduction in levels of TTHMFP and 20% reduction in TOC levels. The preozonation/coagulation/filtration processes was determined to be operationally equivalent to activated carbon adsorption for the removal of THM precursors; it was also determined to be the most cost-effective method of treating organics in the Columbia River water supply.

### c. Plant Design

Approval was given for a 30 mgd water treatment plant to be constructed in four stages of 7.5 mgd each, based on the following processing sequence: preozonation/flash mix/coagulation/-flocculation/filtration and post-chlorination. Design criteria for the preozonation facilities are given in Table XXXIII.

TABLE XXXIII. DESIGN CRITERIA FOR KENNEWICK WATER TREATMENT PLANT PREOZONATION FACILITIES (Cryer, 1986)

| Item | U.S. Units | Initial | Ultimate | Metric Units | Initial | Ultimate |
|---|---|---|---|---|---|---|
| Plant Capacity | | | | | | |
| Design Flow | mgd | 7.5 | 30.0 | $m^3$/day | 28,300 | 113,300 |
| | cfs | 11.6 | 46.41 | $m^3$/sec | 0.33 | 1.33 |
| | gpm | 5,200 | 20,800 | $m^3$/min | 19.70 | 78.62 |
| Ozone Contact Basins | | | | | | |
| No. of basins | | 4 | 16 | | 4 | 16 |
| Detention time @ design flow | min | 10 | 10 | min | 10 | 10 |
| Basin dimensions-inside | ftxft | 14x8 | 14x8 | m x m | 4.2x2.4 | 4.2x2.4 |
| Av. water depth | ft | 16 | 16 | m | 4.8 | 4.8 |
| Basin volume | $ft^3$ | 1,792 | 1,792 | $m^3$ | 50.75 | 50.75 |
| | gal | 13,400 | 13,400 | | | |
| Total basin volume | $ft^3$ | 7,168 | 28,672 | $m^3$ | 203 | 812 |
| Chemical Feed Rate (Max. Dosage @ Design Flow) | | | | | | |
| Ozone plant influent | lb/day | 250 | 1,000 | kg/day | 113 | 454 |
| Chemical Feeders | | | | | | |
| Ozone | lb/day | 2 x 125 | 3 x 250<br>2 x 125 | kg/day | 57 | 3 x 113<br>2 x 57 |
| Chemical Storage Capacity (Max. Dose @ Design Flow) | | | | | | |
| Ozone | No. $O_3$ generators | 2 | 5 | No. $O_3$ | 2 | 5 |
| | Total lbs | 250 | 1,000 | Total kg | 113 | 456 |

At the point of application, ozone dosage rates were 1.5 mg/L (average) and 4.0 mg/L maximum. The contactors provide 10 minutes of detention time.

Raw water total coliform levels are consistently less than 50 per 100 mL. Raw water turbidities are in the range of 1.5 to 2.0 NTU.

### d. Operational Experiences

#### i. General

The new 7.5 mgd treatment plant currently is operated from May through October of each year, when system demand exceeds 10 mgd. For the balance of the year, water demand is about 8 mgd. This can be satisfied by the Ranney Collector system, which operates at lower cost than the new treatment plant.

#### ii. Water Quality

Kennewick's new Columbia River Water Treatment Facilities came on-line in 1980. Generally, the City and the service area customers have been satisfied with the quality of water provided. Treated river water has a higher customer acceptance, judging by the limited number of complaints, than Ranney Collector water alone.

THM analyses of the new treated water and chlorinated Ranney Collector water indicate that the plant has been able to maintain the TTHM concentration below the current 100 ug/L standard, while the quality of water from the Ranney Collector system remains very similar to the levels determined during pilot plant studies for raw Columbia River water. The City's Ranney Collector waters have had an average THM concentration of approximately 107 ug/L, while the ozone treatment plant water has averaged approximately 14 ug/L.

#### iii. Applied Ozonation Dosages - Dissolved Ozone Residuals

Applied ozone dosage rates have ranged from 1.7 to 2.5 mg/L. Until 1983, ozone residual levels were maintained at approximately 0.5 mg/L exiting the contactor. In 1983, the City installed a dissolved ozone analyzer to control the ozone dosage, which has resulted in lowering the dissolved ozone residual concentrations to 0.1 mg/L, thus saving ozone, and still control biological growth in the filters and basins prior to chlorination.

## iv. Ozone Equipment Operational Experience

Operationally, the ozone generation equipment has performed very well. The compressors have required only preventive maintenance. The ozone generators have required the replacement of only three burned out tubes during the first six years of operation. The major maintenance problem appears to be tube fouling which was found to be a result of high moisture in the feed gas. This situation was caused by two extenuating circumstances. After several years of operation, it was discovered that the refrigerant air dryer unit had developed a small leak which reduced the effectiveness of the air preparation system. It was then determined that the absorptive medium in the desiccant drier must be replaced when its regeneration capacity is reduced to 40% of its originally specified capability. Cleaning of dielectric tubes has become an annual maintenance procedure.

The only other significant operational problems concerned the ozone contactors. Excess foaming and scum production can occur during spring and late summer (algae destruction, primarily). This may require the installation of surface skimmers and froth spray. In addition, the stainless steel tubes holding the ceramic diffusers corrode after about two to three years of use, and must be checked and occasionally replaced when the diffusers are cleaned.

## v. Costs Of Ozonation

The Kennewick facility is able to produce ozone at approximately $0.20/lb. However, Cryer (1986) notes that the ozonation system has never been operated at 100% of the high voltage output, and that ozone generation efficiency has averaged approximately 16-17 kWh per pound of ozone produced.

Based upon the City's very limited experience in operating the facility during periods of time when the ozonation system has been off-line, the plant operator believes that the addition of ozone prior to flocculation/filtration results in a savings in flocculation chemicals of approximately 10%.

Currently, the treatment plant is producing finished water at a cost of approximately $14.10 per million gallons ($0.141/1,000 gallons).

### e. Implications for Proposed Surface Water Treatment Rule Disinfection Conditions

During the May/October period of plant operation, the temperature of the waters treated is approximately 20°C. With a 10 minute ozone contacting time, and assuming an average residual ozone concentration of 0.5 mg/L (as was the case until 1983), the CT value of 5 was being obtained, compared with a value of 1.5 required (Table IIA) by the proposed SWTR for 99.9% inactivation of Giardia lamblia cysts and 99.99% inactivation of enteric viruses at 20°C. On the other hand, because the Kennewick plant filters (thereby providing 2-logs of Giardia inactivation), only a single log of additional Giardia inactivation is required. This means (Table IIB) a CT value of less than 0.7, which corresponds to an ozone contact time of only 1.4 minutes.

After filtration, gaseous chlorine is added. A residual of 0.6 mg/L free chlorine is maintained for 60 minutes at pH of approximately 8.0. The contribution of chlorination to the required disinfection CT value thus is 36. From Table IIA, the CT value for chlorine at pH 8.0 and 20°C is 101.

Therefore, maintenance of the 0.5 mg/L ozone residual for 10 minutes provides over 300% of the required disinfection capability, without reliance on the post-chlorination. In addition, post-chlorination provides a supplemental 36% disinfection credit (36/101).

However, since 1983 the ozone residual concentration leaving the ozone contact chambers has been reduced to 0.1 mg/L. Assuming this ozone concentration is present throughout the 10 minutes of ozone contacting, a CT value of only 1 is obtained, versus the 1.5 required by Table IIA. This means that only 67% of the disinfection capability is provided by the preozonation step to achieve 99.9% inactivation of Giardia, but 130% of the inactivation required to obtain only a single log additional inactivation because of the filtration capability. The 60 minute chlorine contact time at pH 8.0 (0.6 mg/L) provides an additional 36% of the required disinfection. This means that the plant currently provides at least 100% of the amount of disinfection stipulated under the proposed Surface Water Treatment Rule, disregarding the contribution of filtration.

## B. UV RADIATION CASE HISTORY

### 1. Ft. Benton, Montana [2]

### UV Radiation for Primary Disinfection

#### a. The Problem

The City of Ft. Benton, MT takes water from the Missouri River and treats it in a 20-30 year old filtration plant. This plant needed to be upgraded. Costs for installing a new filtration plant were deemed to be excessive.

#### b. The Solution

A new 2 mgd peak flow treatment plant was installed in mid-1987. Water is drawn through Ranney Collectors installed 20-25 feet below the river bed. This allows the river bed to be the filter. Turbidities of water entering the treatment plant average 0.08 NTU. No *Giardia* cysts have been found in the filtered water.

Plant intake water is treated with UV radiation for primary disinfection, then chlorinated for residual. If chlorination were to be relied on for primary disinfection, a 2-hour contact time would be required by the State authorities. Even a 30-minute contact time would require two-stage pumping with long concrete pipes to provide sufficient contact time.

After primary UV disinfection, the water is chlorinated to a 1 mg/L residual with no contact time. The water being chlorinated is quite clean, in that the applied chlorine dosage is just over 1 mg/L. The pH is about 7.4 and the water temperature is approximately 20°C year around.

The entire water treatment process is housed in a 32 x 32 ft building.

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[2] The author is indebted to Fred Zinnbauer of Aquionics, Incorporated, Erlanger, KY (supplier of the UV radiation equipment) and to Gary Swanson, Project Engineer at Robert Peccia Associates, Helena, MT, consultants for this project, for information on this plant.

### c. UV Radiation Conditions

The UV disinfection system consists of six irradiation chambers, two control cabinets with alarms, chart recorders, relays, hour-run meters, lamp and power on-lights, six thermostats, electrical door interlocks, mimic diagrams, and six UV intensity motors measuring total UV output.

Four irradiation chambers are on-line at all times, with two chambers reserved for backup. The alarm system is tied into the automatic butterfly valves to provide for a fully automatic backup system. Each irradiation chamber contains one 2.5 kW mercury vapor, medium pressure arc tube, generating UV radiation at 253.7 nm.

The initial UV dosage is 41,000 uW sec/cm$^2$ at maximum water flow (1,650 gal/min) through each irradiation unit. Expected arc tube life is 4,500 operating hours providing a minimum UV dosage of 25,000 uW sec/cm$^2$. These conditions are designed to reduce concentrations of E. coli organisms by a minimum of 5-logs ($10^5$ reduction).

The UV irradiation system is interfaced with the telemetry control system activated when the low tank pump start set-point is activated on the set-point controller. Sufficient warmup time is maintained before pump startup is initiated. The UV system is deactivated once the high tank stop set-point is activated on the set-point controller and the pump stops running. Sufficient time delay is built into the system to ensure that water flow is completely stopped before the UV system is deactivated.

A fully automated backup system is provided. Each bank of three irradiation chambers has two units on-line at all times, with the third unit serving as backup. In the event that the UV intensity drops below acceptable limits (20,000 uW sec/cm$^2$) in any of the chambers, the automatic butterfly valve will close, stopping flow through the chamber and the automatic butterfly valve on the standby unit will open. The alarm system also is activated if UV intensity drops below acceptable limits in any of the chambers. The UV alarm system is interfaced with the automatic dialer and alarm system. Replacement of the UV lamps is quite simple, requiring no more than a few minutes.

### d. Costs

Total equipment costs for the 6-unit UV irradiation system with butterfly valves was $74,587.

### e. Operating Experience

The new Ft. Benton water treatment plant started up in July 1987; there is no operational data yet available

## C. CHLORINE DIOXIDE CASE HISTORIES

### 1. Evansville, Indiana (Lykins & Griese, 1986) Predisinfection for THM Control

#### a. The Problem

Because of the November 1979 amendment to the National Interim Primary Drinking Water Regulations (U.S. EPA, 1979), the Evansville (Indiana) Water and Sewer Utility was faced with reducing the levels of trihalomethanes in their finished drinking water. At the time, raw water was being prechlorinated and treated with alum prior to primary settling, treated with lime (to pH = 8), passed through secondary settling, fluoridated, rapid sand filtered, then post-chlorinated before passage into the clearwell. The treatment process was conducted in two separate 30 mgd treatment lines (total production 60 mgd), and THM levels exceeded the THM standard of 100 ug/L. Prechlorination doses averaged 6 mg/L. Distribution system residence time averages three days.

#### b. Pilot Plant Study

With the assistance of a cooperative agreement from the Environmental Protection Agency (CR811108 - Sept. 1983), the Evansville utility initiated research to evaluate the use of chlorine dioxide in a 100-gal/min pilot plant adjacent to the full-scale plant. One train of the full-scale treatment plant served as the control for the pilot plant study.

The pilot plant study was conducted in two phases, optimization, and long-term. Chlorine dioxide was substituted first for prechlorination, then for post-chlorination. GAC adsorption also was evaluated prior to the post-chlorination step.

##### i. Optimization Phase

If predisinfection was eliminated and the pilot plant effluent was disinfected and stored three days (to simulate distribution system residence time), TTHM concentrations averaged 141 ug/L with chlorine post-disinfection (2.5 mg/L residual chlorine concentration), and 1.2 ug/L with chlorine dioxide post-disinfection (1.9 mg/L residual).

Predisinfection with chlorine dioxide to maintain a residual through the pilot plant did not increase the THM concentration and provided adequate disinfection. The $ClO_2$ residual decreased from 4 to 0.3 mg/L through the pilot plant.

### ii. Long-Term Evaluation

In this phase the pilot plant procedures were evaluated during each season of the year to determine the extent of seasonal effects. In this phase of the study, pre-chlorine dioxide disinfection (1.1 mg/L average applied dosage) reduced the amount of THMs formed during post-chlorination by approximately 60%. The concept of post-disinfection with chlorine dioxide was abandoned because of the difficulty in maintaining a disinfectant residual in the distribution system (three days average residence time), keeping in mind that the current EPA recommendation is that total oxidants from application of chlorine dioxide should not exceed 1 mg/L in the distribution system. The average chlorine residual concentration in the clearwell was 2.1 mg/L.

### c. The Full-Scale Plant

Based on data obtained from the pilot plant study, Evansville utility officials concluded that the MCL for TTHMs would be exceeded if the then-current treatment was not altered. Changing the primary disinfectant from chlorine to chlorine dioxide was judged to be the most effective procedure for control at the least cost. A separate building was constructed to house the chlorine dioxide generation facility. One portion contains the $ClO_2$ generator, a second portion houses two 1-ton cylinders of chlorine.

This installation is capable of generating 14.24 lbs of $ClO_2$ per hour, which can be divided in any proportion between the two halves of the treatment plant. Gaseous chlorine and 25% $NaClO_2$ solution are delivered to the chlorine dioxide reactor under partial vacuum generated by an eductor. Both reagent flows are controlled by flow-rate meters, and the system is designed to shut down if the eductor water supply fails or if chemical feed lines break.

This production rate has been achieved with over 95% conversion to $ClO_2$ over the first 18 month period of operation.

### d. Operating Experience

Chlorine dioxide began being added as a predisinfectant prior to any additional chemical treatment in August 1983. The $ClO_2$ produced is divided evenly between the two treatment lines. During the first five months of use, various $ClO_2$ dosage levels were used to determine the resultant reductions in THM concentrations, to gather data on what percentage of the $ClO_2$ dosage would appear as total oxidant residuals in the finished water, and to review the general operation of the entire system.

During this period, only one major problem was encountered. Brass corporation cocks used to connect the PVC $ClO_2$ feed lines to the raw water influent piping were oxidized by the concentrated disinfectant. This oxidation and subsequent leaking of $ClO_2$ solution resulted in temporary disruption of the new treatment technique. The problem was resolved by sliding a section of PVC pipe through new corporation cocks into the main stream of the raw water lines. This modification permitted the PVC piping to serve as an inductor while preventing direct contact of the brass corporation cocks with concentrated $ClO_2$ solution.

Since the implementation of the treatment change, total oxidant levels from chlorine dioxide have been maintained consistently below the 1.0 mg/L recommended by the U.S. EPA. With an average applied $ClO_2$ pretreatment dosage of 1.2 mg/L, total oxidant concentrations in the finished water have averaged 0.5 mg/L. These data show that approximately 42% of the $ClO_2$ dosage is present as total oxidant.

Since the installation of predisinfection with chlorine dioxide at Evansville, annual TTHM levels in the distribution system have been maintained between 50 and 80 ug/L.

### e. Implications of the Proposed SWTR

Raw water turbidities at Evansville average 20.6 NTU and raw water total coliform levels are in the range of 3,400 to 5,400 per 100 mL. The filtration system provides 2-logs of *Giardia* and virus inactivation. However, because of the higher raw water total coliform levels, EPA recommends (U.S. EPA, 1987e) that disinfection be provided to attain 99.9% inactivation of *Giardia* and 99.99% inactivation of viruses.

Chlorine dioxide predisinfection at Evansville employs a dosage of 1.2 mg/L, followed by chlorination in the clearwell at an average concentration of 2.1 mg/L. Although the contact time after adding $ClO_2$ is not stated in the reference, consideration of the CT value of 20 at 20°C (Table IIA) and an average $ClO_2$ concentration of 1.0 means that a 20 minute contact time would provide 99.9% inactivation of *Giardia* cysts and 99.99% inactivation of viruses, independently of the added degree of disinfection which can be credited to post-chlorination.

With respect to post-chlorination, at an average 2.1 mg/L chlorine residual in the clearwell at pH 8 (CT value = 101 at 20°C) means that a contact time of 48 minutes would be required to provide 99.9% inactivation of *Giardia* cysts and 99.99% inactivation of viruses. If only a 30-minute clearwell contact time is provided, still 63% of the required disinfection is provided in the clearwell.

### 2. Hamilton, Ohio (Augenstein, 1974; Miller et al., 1978; U.S. EPA, 1983)

### Primary/Secondary Disinfection With Chlorine Dioxide

#### a. The Problem

In 1956 a 15 mgd lime softening plant began operating in Hamilton, OH treating groundwater (18 wells, 200 ft deep). Chlorine was used as the sole disinfectant when the plant started operating. However, because of customer complaints of chlorinous tastes and odors, a change was deemed necessary. Chlorine dioxide was tested, and in 1972 this material was substituted for chlorine for primary and secondary disinfection.

#### b. The Treatment Process

Hamilton's treatment process in 1987 is as follows: aeration, lime addition, flash mixing, sedimentation, recarbonation (with food grade $CO_2$), filtration, fluoridation (sodium silicofluoride), disinfection (with $ClO_2$), clearwell storage. Raw water turbidities are below 1 NTU, and raw water total coliforms are less than 1 per 100 mL.

#### c. Generation of Chlorine Dioxide

Chlorine dioxide is generated by mixing 37% aqueous sodium chlorite and aqueous chlorine in a ratio of 1:1 by weight (2 lbs of each reagent per million gallons of water to be disinfected). This provides an applied $ClO_2$ dosage of 0.25 mg/L. Chlorine gas is delivered to the site in 150-lb cylinders. Aqueous $NaClO_2$ solution (37%) is delivered in 200-lb drums.

The chlorine dioxide generation system consists of one plant-fabricated reactor vessel for $ClO_2$ production, one peristaltic pump for $NaClO_2$ solution, two chlorinators (one serves as standby). Two 150-lb liquid chlorine cylinders are positioned next to the chlorinators. The weight of the cylinder contents is measured by a scale. Switchover from one cylinder to the other is manual. PVC tubing is specified between the chlorinator and $ClO_2$ reactor vessel; heavy Tygon tubing transports the $NaClO_2$ solution from the drum to a small plastic day-tank and to the reactor vessel. This Tygon tubing loses its rigidity and must be replaced after about a month's use. The semi-transparent day tank allows visual inspection of the level of liquid $NaClO_2$ and thereby enables the operator to maintain an acceptable suction head on the peristaltic pump.

The chlorine dioxide reactor vessel is constructed of Schedule 80 PVC piping, 18 inches high and approximately 6 inches in diameter. The vessel is filled with PVC rings, 1-inch in diameter. The chamber is opaque except for the sight glass mounted in-line on the discharge piping. A white card is positioned behind the sight glass for inspection of the $ClO_2$ color.

Applied dosage of $ClO_2$ in the clearwell is 0.25 mg/L. The residual leaving the clearwell is approximately 0.15 mg/L, and is 0.10 mg/L at the extremities of the distribution system.

### d. Effects of Installation of Chlorine Dioxide

Prior to installation of $ClO_2$, customers had complained about brown stains (iron) during washing of clothes. When $ClO_2$ treatment was initiated, brown slimes were loosened from the mains. Plant personnel then flushed the distribution system. Shortly thereafter, the brown stain problems disappeared, and complaints ceased. Plant personnel attributed the source of the problem to *crenothrix* and *leptothrix* bacteria (iron bacteria) that had been present in the extremities of the distribution system before introduction of chlorine dioxide.

Since 1972, $ClO_2$ has been the sole disinfectant in Hamilton's drinking water.

### e. Costs for Chlorine Dioxide

In 1977, the costs for $ClO_2$ in Hamilton were determined (Miller et al., 1978) to be about 3.6¢/capita/year. Chlorine and $NaClO_2$ together cost $6,540/yr (1977). Total chemicals costs in 1977 for the finished water averaged 19¢/1,000 gal; the fraction due to $ClO_2$ was considered negligible. The operating and maintenance costs for $ClO_2$ generation at Hamilton were estimated to be less than $50/yr in 1977. The plant-fabricated $ClO_2$ reactor, piping, hardware, and installation were estimated by the plant supervisor to cost around $400 in the 1977 market. Installation was done by plant personnel. The peristaltic pump for $NaClO_2$ solution cost less than $200 (1977). To this must be added the cost of the two chlorinators ($600).

### f. Implications for the New SWTR CT Values

Although the Hamilton raw water is groundwater, and therefore will not be subject to the requirements of the proposed Surface Water Treatment Rule (U.S. EPA, 1987a), it is interesting to consider the effects if such disinfection requirements as listed in Table IIA were to be levied on this water supply system.

Chlorine dioxide is added to the Hamilton water in applied doses of 0.25 mg/L as it enters the clearwell. The water temperature is about 20°C year round, and the pH is 9.4 to 9.5. Hamilton's first customer is located about 0.5 mile from the plant. Thus there is very little contact time in the distribution system. The plant filters efficiently, and therefore only 1-log additional inactivation of *Giardia* cysts and 2-logs inactivation of viruses need be provided by the chlorine dioxide. Table IIB shows that at 15°C, a CT value of 9 will provide the required degree of disinfection.

The Hamilton clearwell holds 500,000 gallons. During periods of high water use, water is produced at the rate of 19 mgd. In periods of low water use, only 8 mgd are produced. Thus the contact time in the Hamilton clearwell ranges from 30 to 90 minutes, at the high and low production rates, respectively. Assuming that the average concentration of $ClO_2$ in the clearwell is 0.2 mg/L, then the CT values provided are 6 and 18, respectively.

Thus the current disinfection conditions using chlorine dioxide meet the proposed CT requirements, except at the most rapid production of water, when only 50% of the disinfection capability is provided by $ClO_2$ in the clearwell. However, simply doubling the $ClO_2$ dosage during periods of highest flow will provide the additional amount of disinfection required by the proposed SWTR.

### 3. Galveston, Texas (Myers et al., 1986)

### Preoxidation With $ClO_2$
### Post-Disinfection With $ClO_2$ + Chloramine

#### a. The Problem

The Galveston County Water Authority (GCWA) owns and operates an 18 mgd capacity water treatment plant in Texas City, TX, currently (1986) producing 12 mgd of finished water from the Brazos River. Raw water characteristics include high color, variable turbidities (68-111 NTU), high organic contents, high iron (2.7-3.8 mg/L), and seasonally high algae content, sometimes reaching levels of 5,000 blue/green algae/mL. Such high algae and organic contents create the potential for unpalatable tastes and odors to develop during treatment and distribution.

Total trihalomethane formation potentials for Brazos River water, measured periodically during September 1983 through April 1984 (20-day chlorination period), were in the range of 400 to 650 ug/L. Finished water THM concentrations measured during the same period were in the range of 180 to 350 ug/L. During periods of intermittent raw water algae blooms and associated high organic carbon contents, numerous consumer complaints were received regarding tastes and odors.

These problems prompted an investigation of alternative disinfectant strategies.

### b. The Original Treatment Process

The treatment process included addition of cationic polymer for primary coagulation, lime for pH adjustment, prechlorination for taste and odor control, and ferric sulfate as a flocculant aid prior to upflow reactor/clarifiers. These provide the dual function of flocculation and sedimentation. Dual media filtration follows, then disinfection (chlorination to a 2.4-5.0 mg/L total available chlorine residual in the finished water), and fluoridation.

### c. Study of Alternatives

Chloramines and chloride dioxide were selected for further study and pilot plant testing. Ozone was eliminated from further study because of implementation considerations. Also, ozone does not maintain a residual during distribution, and therefore would require the use of a secondary disinfectant anyway. Chlorine dioxide for both preoxidation and post-disinfection achieved the goals of GCWA better than did chloramines (poor preoxidant).

Preoxidation/post-disinfection combinations were studied in the following Phases:

1) Chlorine/chlorine

2a & b) Chloramine/chloramine

3) Chlorine dioxide/chlorine

4) Chlorine dioxide/chlorine dioxide

5) Chlorine dioxide/combined chlorine + chlorine dioxide, and

6) Chlorine dioxide/combined chloramine + chlorine dioxide.

### i. Study Results

#### Phase 1: Chlorine - Chlorine

Finished water exhibited intermittent algae-related taste and odor, and THM levels were in excess of federal standards (350 ug/L). Bacterial quality was excellent. This approach was abandoned.

#### Phases 2a and 2b: Chloramine - Chloramine

Phases 2a and 2b employed chlorine:ammonia weight ratios of 3:1 and 7:1, respectively. Although THM levels were about 60 ug/L, bacterial counts for coliforms demonstrated that confluent growth was occurring on several cultures, indicating that inadequate residual was being maintained in the distribution system (3:1 chlorine:ammonia ratio). This approach was abandoned.

The experiments were repeated using the 7:1 chlorine/ammonia ratio. Acceptable bacterial quality was achieved, but numerous taste and odor complaints were received during this period. This approach was abandoned.

#### Phase 3: Chlorine Dioxide - Chlorine

Chlorine dioxide was installed in May 1984, using a generator with a conversion efficiency (chlorite ion to $ClO_2$) of approximately 80%. After $ClO_2$ preoxidation, the clarified water showed no traces of THMs. No taste and odor complaints were received, despite very high raw water algae counts (up to 5,000 blue/green algae/mL). However, finished water THM levels sometimes persisted above 100 ug/L.

In November 1984, a chlorine dioxide generator with a 98+% conversion efficiency was installed, and this phase was continued for an additional two months. THM levels averaged 102 ug/L), and no taste and odor complaints were received. This approach was abandoned.

#### Phase 4: Chlorine Dioxide - Chlorine Dioxide

This approach of using chlorine dioxide both as the preoxidant and post-disinfectant was authorized on an interim basis by the Texas Department of Health in early March 1985 with the stipulation that a maximum $ClO_2$ residual of 1.0 mg/L be maintained and that finished water quality be monitored throughout the distribution system.

Finished water THM concentrations during the test period averaged 60 ug/L, and finished water turbidities were the lowest of any of the alternative disinfectant scenarios. Bacterial counts generally were excellent, but intermittent elevated bacterial counts were noted at three different points in the distribution system: at the clearwell, and at locations 2 and 5 miles from the plant.

Additionally, the bacterial species distribution also changed upon $ClO_2$ disinfection, both at the plant and in the distribution system. Bacterial counts displayed a shift from orange to yellow-staining gram negative (-) rods to white-staining gram positive (+) rods, similar to slime-forming Bacillus (sp.).

This approach, although promising, also was abandoned.

### Phase 5: Chlorine Dioxide - Combined Chlorine + Chlorine Dioxide

Phase 4 was repeated except that chlorine was applied in conjunction with $ClO_2$ until the bacteria could be identified. Excellent bacterial quality was obtained. The bacterial plate counts remained at or below the guideline of 500 colonies per 100 mL for all monitoring locations. The shift in bacterial species distribution continued as the plate counts decreased, so that over 95% of all colonies examined were either yellow gram (-) rods or white gram (+) rods.

Finished water THM levels rose to an average of 81 ug/L. This approach was rejected, in favor of Phase 6.

### Phase 6: Chlorine Dioxide - Combined Chloramine + Chlorine Dioxide

This phase was implemented on December 6, 1985. With this post-disinfection combination, finished water THM levels averaged 68 ug/L, and the bacteriological quality remained excellent. No coliforms were found in the clearwell or in the distribution system during this phase, and bacterial counts have ranged from less than 1 to 30 colonies per 100 mL. Of those colonies identified, over 95% were the white-staining, gram (+) Bacillus (sp.) variety with less than 1% belonging to the orange-staining gram (-) type.

### d. The Results

Preoxidation with chlorine dioxide and post-disinfection with $ClO_2$ in combination with either chlorine or chloramines has provided effective taste and odor control, maintained an active disinfectant residual and mitigated THM formation (to a current level of about 68 ug/L).

Chlorine dioxide preoxidation has proven to be an excellent algicide and biocide. The effectiveness of $ClO_2$ in removing algae in flocculation/sedimentation has been demonstrated in a decrease in filter fouling and improved finished water turbidities since implementing its use.

Odors experienced at the flocculating clarifiers and taste and odor complaints in the distribution system have been reduced. The unexpected benefit of improved treatment plant performance has been maintained for at least the first seven months of operation of the treatment modifications. Finished water turbidities decreased from an average range of 0.3 to 0.65 NTU during 1983 (chlorine pre- and post-treatment) to 0.09 to 0.2 NTU in 1986.

Bacterial counts using the membrane filter method for coliforms have declined to excellent levels. Since the advent of $ClO_2$ post-disinfection, all bacterial counts obtained from samples collected at the GCWA distribution point have been below 30 colonies/100 mL, and all but two samples have been below 10 colonies/100 mL. This indicates a substantial residual present at that distribution system point. The bacterial counts obtained from the GCWA distribution system are continually below the guideline of 500/mL, and often are below 5 colonies/100 mL, indicating the maintenance of a good, active residual.

The Galveston County Water Authority has successfully implemented the first chlorine dioxide disinfection program in the State of Texas.

## C. CHLORAMINE CASE HISTORIES

### 1. Bloomington, Indiana (Singer, 1986)

### Prechlorination, Post-Chloramination

#### a. The Problem

Bloomington takes its water from a lake having TOC levels of 4-6 mg/L. This water is treated by conventional coagulation with alum, flocculation, sedimentation, and filtration through pressure filters. Prior to September 1984 the utility applied chlorine to the raw water and again ahead of the pressure filters. Aver ge chlorine dosages were 1.8 and 1.0 mg/L, respectively. Typical average TTHM concentrations reported by the utility as part of its quarterly compliance monitoring program were as follows:

| | | |
|---|---|---|
| March | 1983 | 77 ug/L |
| June | 1983 | 168 ug/L |
| Sept | 1983 | 142 ug/L |
| Dec | 1983 | 50 ug/L |
| March | 1984 | 79 ug/L |
| May | 1984 | 113 ug/L |

It is clear that the current 100 ug/L TTHM running annual average standard was being exceeded.

### b. The Solution

In September 1984, the Bloomington water utility changed from post-chlorination to post-chloramination. An average 0.54 mg/L of ammonia was applied along with 1.5 mg/L of chlorine ahead of the pressure filters. The desired residual chlorine concentration leaving the plant of 1.0 mg/L of free chlorine was changed to 1.5 mg/L of combined chlorine.

### c. Performance

Quarterly compliance monitoring data for TTHMs subsequent to the changeover are as follows:

| | | |
|---|---|---|
| Sept. | 1984 | 47 ug/L |
| Dec. | 1984 | 24 ug/L |
| Feb. | 1985 | 43 ug/L |
| April | 1985 | 56 ug/L |
| Aug. | 1985 | 57 ug/L |

Clearly, TTHM concentrations have been brought down to about 50 ug/L from well over 100 ug/L.

Table XXXIV summarizes THM and TOX (Total Organic Halide) data for samples collected as major points in the treatment system when chlorine alone was used for pre- and post-treatment. The data show that TOX levels increased in parallel with increases in TTHM levels. Table XXXV summarizes similar data taken using combined chlorine residuals. These data show that although the TTHM formation ceases after the addition of ammonia, the production of TOX continues, although at a greatly reduced rate. This illustrates that as EPA sets MCLs for other halogenated organic materials than THMs, utilities opting for post-chloramination must plan to determine the makeup of their TOX fraction.

Since switching to post-chloramination, the utility has experienced no adverse effects in operations or in finished water quality. According to distribution system monitoring records, the microbiological safety of the water has been maintained.

TABLE XXXIV. SUMMARY OF THM DATA AT BLOOMINGTON, INDIANA WITH FREE CHLORINATION 8/16/84 (Singer, 1986)

| Sampling Point | Residual Free Chlorine, mg/L | TOC mg/L | TTHM ug/L | TOX ug/L |
|---|---|---|---|---|
| Raw Water | --- | 4.3 | 1 | 23 |
| Settled Water | 0.25 | 3.6 | 48 | 127 |
| Filtered Water | 1.0 | 2.4 | 81 | 205 |
| Dist. System #1 | 1.8 | --- | 110 | 291 |
| Dist. System #2 | 0.65 | --- | 151 | 363 |

TABLE XXXV. SUMMARY OF THM DATA AT BLOOMINGTON, INDIANA WITH POST-CHLORAMINATION 8/26/85 (Singer, 1986)

| Sampling Point | Residual Chlorine, mg/L | TOC mg/L | TTHM ug/L | TOX ug/L |
|---|---|---|---|---|
| Raw Water | --- | 4.1 | 0 | 17 |
| Settled Water | Trace, Free | 2.8 | 53 | 94 |
| Filtered Water | 1.2 Combined | 2.8 | 55 | 91 |
| Dist. System #1 | 1.0 Combined | --- | 52 | 115 |
| Dist. System #2 | 0.9 Combined | --- | 57 | 116 |

### 2. Philadelphia, Pennsylvania (McKeon et al., 1986)

Pre-Chlorine Dioxide + 1-Hour Prechlorination
Post-Chloramination

This is a case history which is still evolving, but one which has resulted in modifications to attain current regulatory and water quality objectives. However, the types of studies which have been conducted by the Philadelphia Water Department point to the directions this utility probably will take in response to continued tightening of federal regulations and changes in water quality.

### a. The Problems

The Baxter Water Treatment Plant (formerly called Torresdale), was built in 1960 on the site of a slow sand filtration plant that had been in service since 1903. The current plant is rated at 282 mgd, and supplies potable water to over 800,000 people, from the Delaware River by conventional treatment.

Chemicals fed routinely include chlorine, ferric chloride or ferrous sulfate, lime, fluoride, and ammonia. Powdered activated carbon is fed on demand for control of taste and odor events, and chloride dioxide is fed currently for THM control and reduction of tastes and odors. The $ClO_2$ feed system was incorporated in the original plant design in the 1950s to oxidize phenolic compounds found in the watershed. Since that time, the sources of phenol have been eliminated, and the $ClO_2$ feed system has found use as part of the program to reduce concentrations of trihalomethanes.

Prior to 1976, the Baxter plant practiced breakpoint chlorination at the raw water basin and maintained free chlorine in the distribution system. From raw water chlorination to the consumer, a total of 96 hours of free chlorine contact time normally elapsed.

Initial analyses for THMs in 1978 showed peak concentrations above 300 ug/L with a running annual average of 140 ug/L. In light of these results, the Philadelphia Water Department began to reevaluate its disinfection strategies. The selection of an alternative disinfectant strategy at the Baxter plant not only must take into consideration bacterial kills, but taste and odor control, suppression of algae, corrosion control, residual duration, and economics.

This case history will review Philadelphia's experiences over ten years in modifying chlorination practices, and the problems which surfaces with reduction of chlorine contact time.

### b. Process Modifications

Initial efforts to reduce formation of THMs concentrated on reduction in free chlorine contact times. From the original 96-hour free chlorine contact time, today (1986) chlorine contact time has been reduced to 1-hour.

### i. Chloramination of Finished Water (Reduction of Free Chlorine Contact Time from 96-hours to 24-hours)

Chloramination of the finished water was initiated in 1976. Ammonia was added to convert free chlorine to monochloramine, to yield a longer lasting residual in the distribution system, to improve the organoleptic properties of the water, and to reduce the corrosion rates associated with the use of free chlorine. Adequate disinfection was assured by maintaining a 2-3 mg/L free chlorine residual throughout the plant treatment process.

Trihalomethane formation within the treatment process was reduced by 40% under summertime conditions in comparison to the ultimate (96-hour) THMFP reached previously (from 231 to 174 ug/L).

### ii. Reduction in Chlorine Treatment at Raw Water Basin

A gradual phasing out of chlorine addition at the raw water basin inlet took place from 1976 through 1979. Whereas in 1975, 60 lbs per million gallons of chlorine was added at the intake, by the end of 1979, chlorine addition was limited to 20-30 lbs/million gallons. From 1977 to 1979, the marginal chlorination of the intake followed by five hours of free chlorine contact time in the floc/sedimentation basins and filters produced summertime average THM concentrations of 200 ug/L and yearly averages of 140 ug/L. While this treatment regimen produced positive results in the control of algae blooms in the raw water basin and minimization of taste and odor events, its debit was high formation of THMs. The decreased use of chlorine in the raw water basin also had the effect of reducing the amount of chlorine loss due to evaporation, and thus the quantity of chlorine used.

### iii. Utilization of Chlorine Dioxide at Raw Water Basin Inlet (5 Hours Free Chlorine Contact Time)

Beginning in 1980, routine use of chlorine at the raw water intake basin was abandoned. In its place, chlorine dioxide was added in dosages between 0.5 and 1.0 mg/L. Summertime THM values thus were reduced from 200 ug/L to 140 ug/L. This treatment was sufficient to control algae, and thus tastes and odors, at all times except during the spring algae bloom. For that period of time, breakpoint chlorination of the intake water and/or 100-200 lbs of powdered activated carbon per million gallons is required to eliminate vegetative tastes and odors.

### iv. Installation of a New Chlorine Application Point (One Hour Free Chlorine Contact Time)

In the fall of 1980, a chlorine application point was installed in the "applied to filters" channel which allowed for increased flexibility in the use of chlorine. Free chlorine contact time was reduced from five hours to one. Chlorine was added at the rapid mix to barely achieve breakpoint and achieve a residual which dissipated within a few minutes. Chloramines were carried across the floc/sedimentation basins. Sufficient chlorine then was added at the new application point to achieve a free chlorine residual of 1.5-2.0 mg/L. This residual was converted to chloramines one hour later as the water flow left the filter building.

This treatment regimen gave adequate control of taste and odor, except for the previously mentioned outbreaks associated with spring algae blooms, which forced reversion back to free chlorine at the intake. THM formation, with only one hour free chlorine contact time, resulted in summertime values averaging 100 ug/L with a yearly running average of 60 ug/L.

### v. Ten Minutes Free Chlorine Contact Time

A plant trial was carried out in November 1982 utilizing a 10-minute chlorine contact time. Results indicated that satisfactory disinfection could be achieved with only chloramines carried through the floc/sedimentation basins when water temperature was below 60°F. This strategy was initiated on a plant-scale in December 1982. Adequate disinfection was achieved, but periodic taste and odor results were less than satisfactory. Medicinal and chemical taste complaints were received and several large taste and odor events occurred following storms.

THM results under the reduced chlorine treatment reduced running annual average concentrations from 60 to 50 ug/L.

The trial was terminated in December 1983 because the disinfection scheme did not adequately address the taste and odor qualities of the water. Treatment regimen returned to 1-hour free chlorine contact time.

### c. Economics

Realization of 70% reduction in THM concentrations over the ten year period was obtained at minimum cost. The 1978 disinfection cost was $5.01/million gallons; in 1986 the cost was $9.53. Converting the 1986 costs into 1978 dollars, the 1986 adjusted cost is $5.52/million gallons. Cost increases were minimized because the reduced chlorine contact times resulted in less evaporation losses of chlorine, which netted a 20% decrease in the amount of chlorine utilized. This partially offset the increased costs incurred by the use of chlorine dioxide.

### d. Operational Experiences

Free chlorine contact times at the Baxter plant have been reduced from 96-hours in 1975 to 1-hour in 1986. Trihalomethane concentrations in the finished water have been reduced from an estimated annual average of 220 ug/L in 1975 to 60 ug/L in 1986. Treatment strategy is most critical during the spring and summer months when vulnerability to taste and odor events is high and THM formation within the treatment process is accelerated due to warm water temperatures.

### e. For the Future

The near term goal of the Philadelphia Water Department is to reduce the annual running THM concentration average below 50 ug/L, a 15% reduction from current (1986) levels. This can be achieved at minimum expenditure by installation of a pH adjustment point at post-treatment. The existing treatment scheme calls for raising the raw water pH to 8.4 at the rapid mix and carrying this high pH through the distribution system for corrosion protection. Addition of a pH adjustment point at post-treatment will allow for a pH of 7.5 to be used through the floc/sedimentation basins and filters, with pH adjustment to 8.4 after chloramination. Plant scale trials using this treatment regimen yielded a 20% reduction in THM formation (to about 40 ug/L).

If EPA lowers the THM MCL to below 50 ug/L, ozone and/or granular activated carbon become the likely alternatives at the Baxter plant. Extensive laboratory and pilot plant evaluations (Neukrug et al., 1984) have developed conceptual full-scale plant designs incorporating these two treatment techniques.

Estimated annual amortized capital and operating costs for ozone at the Baxter plant, spread over the lifetime of the equipment, are estimated to be about $50/million gallons. The associated costs for GAC post-contacting (15-minute empty bed contact time) with a 75-day regeneration frequency would be about $212/million gallons. This design configuration is capable of producing THM concentrations of less than 10 ug/L.

## IX. SUMMARY RECOMMENDATIONS FOR DISINFECTION STRATEGIES AND FOR THE CONTROL OF DISINFECTION/OXIDATION BY-PRODUCTS

Consideration of all of the preceding discussions, including the case studies, leads to the following general and specific conclusions and recommendations:

### A. For Disinfection

1. From review of EPA's draft Surface Water Rule (U.S. EPA, 1987a) and the National Academy of Sciences recommendations (NAS, 1987), ozone and chlorine should be viewed as the primary disinfectants of choice. However, chlorine can be used only when the THM and TOX formation potentials are sufficiently low, and with the assumption that no other halogenated products are formed in quantities sufficiently high that they will be regulated. UV radiation can be used as a primary disinfectant, but for groundwater only, since it does not provide the required amount of inactivation of Giardia cysts for surface water treatment.

2. For groundwater disinfection, ozone, chlorine, and UV radiation are the primary disinfectants of choice, with the same restrictions on chlorine as noted above.

3. Monochloramine is not recommended by EPA or by NAS as a primary disinfectant because of its very high CT values with respect to Giardia cysts and because inactivation of Giardia cysts with chloramine does not guarantee inactivation of viruses.

4. NAS also recommends against the use of preformed monochloramine and against marginal chlorination as methods of introducing chloramines. Organic N-chloramines, which are even weaker disinfectants than monochloramine, are formed by these chloramination techniques.

5. For surface or groundwater, chlorine is the most effective secondary disinfectant, provided the water is sufficiently clean that significant quantities of THMs and other halogenated organic compounds are not produced.

5. If an MCL is set for chlorine dioxide at 1.0 mg/L, this material can be considered for primary disinfection, and definitely can be employed as a secondary disinfectant. A $ClO_2$ dosage of 1.3-1.5 mg/L will produce residual oxidant ($ClO_2$ + chlorite ion + chlorate ion) levels of ~ 1 mg/L.

6. On the other hand, if an MCL for chlorine dioxide is set at 0.2 mg/L (Table VII), $ClO_2$ will not serve as either a primary or secondary disinfectant. EPA's draft Surface Water Treatment Rule requires maintaining a disinfectant residual of at least 0.2 mg/L throughout the distribution system.

7. If an MCL is set for monochloramine at 2.5 mg/L, it can be used as a secondary disinfectant. However, if an MCL is set at 0.29 mg/L (Table VII), its use as a secondary disinfectant, while not eliminated, will be marginal at best, and will require very close control.

8. If EPA sets low MCLs for both $ClO_2$ and chloramine, chlorine then will become the <u>only</u> practical secondary disinfectant available. In this event, the water will have to be pretreated more efficiently in order to lower TOX precursor formation and allow the use of chlorine as the secondary disinfectant.

9. The National Academy of Sciences (1987) recommends that when chlorine is used as the primary disinfectant, an amount should be used that is sufficient to produce a slight residual of free chlorine above that required to oxidize nitrogen, followed by addition of ammonia to form monochloramine and limit THM formation.

10. CT values for different disinfectants employed in a treatment process are additive. For example, preoxidation with ozone or chlorine dioxide for a non-disinfection application nevertheless provides some CT benefit which can be added to that obtained in the primary and secondary disinfection steps. When attempting to take disinfection credit for ozone, a measurable residual of dissolved ozone must be maintained for a specific contact time.

11. When using ozone for disinfection, contact time must be defined in terms of detention time in the ozone contacting chamber. This is because ozone residuals dissipate rapidly after application of ozone to water ceases.

12. Changing disinfection procedures usually must be made with attention being paid to overcoming other water quality problems, such as color, taste and odor, iron and manganese, synthetic or volatile organic contaminants, etc.

13. Whenever ozone is employed, for oxidation or disinfection purposes, it should be added in the absence of chlorine, chlorine dioxide, or chloramine. This is because ozone oxidizes these three chemicals, and both reagents are mutually destroyed, to no benefit to the water treatment process. When primary disinfection with ozone is followed

by chlorine, chlorine dioxide, or chloramine as the secondary disinfectant, it is important that no residual ozone be present, particularly in the case of chlorine dioxide, for the same reason.

### B. For Controlling Disinfectant/Oxidant By-Products

14. Currently, halogenated by-products are the only compounds being regulated or selected for regulation in the next few years.

15. Attention to minimizing the use of chlorine during disinfection will also minimize the production of disinfection by-products.

16. Conventional water treatment processes should be improved to remove or minimize concentrations of organic precursors of disinfection by-products prior to the addition of chlorine. Preoxidation and activated carbon adsorption are treatment steps which can be effective in this regard. Ozone, potassium permanganate, hydrogen peroxide can be effective preoxidizing agents. Chlorine dioxide also is an effective preoxidant, if its use at 1-1.5 mg/L dosages continues to be allowed.

17. When relying on monochloramine as the secondary disinfectant, close attention should be paid to the TOX levels and the halogenated organic products which are contained in this group parameter.

18. Most current preoxidation applications of ozone are designed to provide only a trace residual of ozone at the exit of the contact chamber. To calculate the disinfection credit of ozone under such conditions requires making assumptions regarding the period of time the ozone residual concentration is established and maintained (if only a single ozone contactor is employed). Satisfying the ozone demand of the water and attaining the desired residual of ozone in a first contact chamber, followed by a second chamber in which the desired residual ozone is maintained, is a more quantitative and reliable disinfection design approach.

19. In plants currently employing ozone for preoxidation using a single contactor, simply increasing the dissolved ozone residual to the level appropriate for the designed ozone contact time and the water temperature can provide at least the major portion, if not all, of the primary disinfection required to guarantee inactivation of _Giardia_ cysts and enteric viruses.

## X. REFERENCES

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# 4

# Chemistry of Chlorination

## FUNDAMENTALS OF CHLORINE CHEMISTRY

### Introduction

This chapter will describe the chemistry of chlorine gas molecules and their reactions when dissolved in aqueous solutions. The purpose of this presentation will be to show all of the fundamental reactions so that the practical application of chlorine to potable water, industrial process water, and wastewater can be better understood and analyzed.

Our knowledge of the fundamental chemistry of chlorination has been enlarged considerably in the past fifty years. This has contributed to significant advancement in the field. However, the more we learn, the more we realize how fortuitous it is that chlorine, applied in its simplest form ($Cl_2$), can be such a potent disinfectant. This phenomenon of chemical simplicity must surely be an important contributing factor to its germicidal efficiency. As a disinfectant, it is without equal, despite its shortcomings.

It is well known that the amount and complexity of pollutants reaching our potable water supplies are increasing at an alarming rate. This has a direct effect on the chemical reactions of chlorine in aqueous solutions. In general it can be said that the following compounds are of significance in their reactions with chlorine, insofar as water and waste treatment are concerned,

1. Ammonia
2. Amino acids
3. Proteins
4. Total organic carbon (TOC)
5. Nitrites
6. Iron
7. Manganese
8. Hydrogen sulfide
9. Cyanides
10. Organic nitrogen

Before discussing the reactions of these compounds with chlorine, it is desirable to become acquainted with how the chlorine molecule is handled as a disinfectant. Chlorine gas is dissolved either directly in water (by a chlorinator) to form hypochlorous acid, or by a specially controlled process in a solution containing caustic to yield a hypochlorite bleach solution. When the latter solution is used as a disinfectant it is diluted with water to form hypochlorous acid, as in the first method. The first part of this discussion will concern the fundamental reaction of chlorine and water and the formation of the oxidizing agent (hypochlorous acid).

## Hydrolysis of Chlorine Gas

When chlorine gas is dissolved in water, it hydrolyzes rapidly according to the following equation:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \qquad (4\text{-}1)$$

The rapidity of this reaction has been studied by many investigators. Complete hydrolysis occurs in a few tenths of a second at 18°C; at 0°C only a few seconds are needed.[1] This unusually rapid rate of reaction is best explained if the mechanism is a reaction of the chlorine molecule with the hydroxyl ion rather than with the water molecule. This can be represented as follows:

$$Cl_2 + OH^- \rightleftharpoons HOCl + Cl^- \qquad (4\text{-}2)$$

The rate constant for this reaction is about $5 \times 10^{14}$ indicating that the reaction occurs at almost every collision of ions.[2] This reaction is of great practical importance because it relates to the chemistry of aqueous chlorine solutions discharging from conventional chlorination equipment. The resulting solution in a chlorinator discharge is limited by design to 3500 mg/liter. At this concentration the most highly buffered injector water would result in a pH of no higher than 3. At this pH the amount of molecular chlorine in equilibrium with HOCl is substantial. Concentrations higher than 3500 mg/liter cause excessive chlorine gas release at the point of application which is extremely undesirable. Likewise if negative pressures exist in the chlorine solution piping, this contributes to the release of molecular chlorine at the point of application. In addition to the degassing effect, the release of gas in the solution piping has been known to adversely affect the hydraulic gradient between the injector and the point of application. Injector systems are usually designed to maintain at least 2 psig at the injector discharge. At this pressure and a temperature of 20°C, the solubility of chlorine in water is only about 7.5 g/liter.[3]

To demonstrate the relationship of the molecular chlorine-hypochlorous acid equilibrium for both buffered and unbuffered water, the following tables have been compiled from a computer printout provided by the Bioengineering Research and Development Lab, U.S. Army, Fort Detrick, Maryland.[4] The results are based upon the $Cl_2$-HOCl equilibrium; the $Cl_3^-$ ion formation from $Cl_2$ and the chloride ion; a mass balance for all chlorine species; and an ion balance on $Cl^-$. Thus the

Table 4-1 Percent Molecular Chlorine and Hypochlorous Acid in a Water Solution Buffered from pH 1–6 at 15°C at Atmospheric Pressure

| | Solution Concentration (mg/liter) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 500 | | 1000 | | 1500 | | 2000 | | 3500 | |
| pH | $Cl_2$ | HOCl | $Cl_2$ | HOCl | $Cl_2$ | HOCl | $Cl_2$ | HOCl | $Cl_2$ | HOCl |
| 1 | 54.30 | 45.65 | 64.67 | 35.25 | 69.94 | 29.95 | 73.29 | 26.57 | 78.91 | 20.89 |
| 2 | 17.66 | 82.31 | 27.41 | 72.52 | 33.95 | 65.93 | 38.78 | 61.05 | 49.70 | 49.97 |
| 3 | 2.48 | 97.51 | 4.73 | 95.25 | 6.79 | 93.17 | 8.68 | 91.26 | 13.57 | 86.28 |
| 4 | 0.26 | 99.72 | 0.52 | 99.46 | 0.77 | 99.20 | 1.02 | 98.45 | 1.76 | 98.19 |
| 5 | 0.026 | 99.74 | 0.05 | 99.71 | 0.078 | 99.68 | 0.104 | 99.66 | 0.181 | 99.58 |
| 6 | 0.000 | 97.68 | 0.005 | 97.67 | 0.008 | 97.67 | 0.010 | 99.67 | 0.018 | 97.66 |

mole percent for HOCl in the following tables is based upon a lengthy and complex cubic equation* which is best described as follows:

$$\text{Percent HOCl} = \frac{100 \times (\text{HOCl})}{[(\text{HOCl}) + (\text{Cl}_2) + (\text{OCL}^-) + (\text{Cl}_3^-)]} \qquad (4\text{-}3)$$

Table 4-1 illustrates what happens in the chlorine solution discharge from a chlorinator ranging in feed rates to produce concentrations varying from 500–3500 mg/liter It also demonstrates the necessity for maintaining a constant high concentration of chlorine (e.g., 1500–2000 mg/liter at a low pH in the generation of chlorine dioxide). The molecular chlorine present in the solution coming in contact with the sodium chlorite provides the impetus for a fast and complete reaction.

Table 4-2 demonstrates the stability of a chlorine water solution buffered with either sodium hydroxide or calcium hydroxide. These figures are of interest for on-site manufacture as well as on-site generation of hypochlorite.

In any hypochlorite solution the active ingredient is always hypochlorous acid.

$$\text{NaOCl} + \text{H}_2\text{O} \longrightarrow \text{HOCl} + \text{Na}^+ + \text{OH}^- \qquad (4\text{-}4)$$

$$\text{Ca(OCl)}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{HOCl} + \text{Ca}^{++} + (\text{OH})^= \qquad (4\text{-}5)$$

When a chlorine solution, such as the solution discharge of a conventional chlorinator (unbuffered), is subjected to negative pressure conditions, the solubility is reduced which usually results in the release of molecular chlorine at the point of

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* This equation is shown in the Appendix

Table 4-2 Percent Molecular Chlorine, Hypochlorous Acid and $OCl^-$ Ion in a Water Solution Buffered from pH 6–9 at 20°C

| | Solution Concentration (mg/liter) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 5000 | | | 7000 | | | 10000 | | |
| pH | $Cl_2$ | HOCl | $OCl^-$ | $Cl_2$ | HOCl | $OCl^-$ | $Cl_2$ | HOCl | $OCl^-$ |
| 6.5 | .0063 | 92.28 | 7.71 | .0088 | 92.28 | 7.71 | .0126 | 92.28 | 7.71 |
| 7.0 | .0017 | 79.10 | 20.89 | .0024 | 79.10 | 20.89 | .0034 | 79.10 | 20.89 |
| 7.5 | .0004 | 54.84 | 45.51 | .0005 | 54.49 | 49.51 | .0007 | 54.49 | 45.51 |
| 8.0 | .0001 | 27.46 | 72.54 | .0001 | 27.46 | 72.54 | .0001 | 27.46 | 72.54 |
| 8.5 | .0000 | 10.69 | 89.31 | .0000 | 10.69 | 89.30 | .0000 | 10.69 | 89.30 |
| 9.0 | .0000 | 3.65 | 96.35 | .0000 | 3.65 | 96.35 | .0000 | 3.65 | 96.35 |

application provided the diffuser is in an open body of water such as an open channel.

For example, at atmospheric pressure and 20°C, the maximum solubility of chlorine is about 7395 mg/liter. However, if the solution is subjected to a negative head of 9 in. Hg the solubility is reduced to about 5560 mg/liter.[4] Therefore, all systems that are not closed should be designed to avoid negative pressure conditions in the chlorinator solution lines.

## Chemistry of Hypochlorous Acid

**Effect of pH.** The next most important reaction in the chlorination of an aqueous solution is the formation of hypochlorous acid. This species of chlorine is the most germicidal of all chlorine compounds with the possible exception of chlorine dioxide.

Hypochlorous acid is a "weak" acid which means that it tends to undergo partial dissociation as follows:

$$HOCl \leftrightharpoons H^+ + OCl^- \qquad (4\text{-}6)$$

to produce a hydrogen ion and a hypochlorite ion. In waters of pH between 6.5 and 8.5 the reaction is incomplete and both species are present to some degree. The extent of this reaction can be calculated from the equation

$$K_i = \frac{(H^+)(OCl^-)}{(HOCl)} \qquad (4\text{-}7)$$

$K_i$, the ionization constant, varies in magnitude with temperature. The values of this constant shown in Table 4-3 have been computed from the acid dissociation constant, $pK_a$, based on J. C. Morris,[5] best fit formula developed in 1966 as follows:

$$pK_a = \frac{3000.00}{T} - 10.0686 + 0.0253T \qquad (4\text{-}8)$$

where $T = 273 +$ degrees centigrade.

Table 4-4 shows the percent undissociated HOCl species for the various temperatures and pH values from 4–11.7. The percent $OCl^-$ ion is the difference between these numbers and 100.

The percent distribution of the $OCl^-$ ion (hypochlorite ion) and undissociated hypochlorous acid can be calculated for various pH values as follows:

$$\frac{(HOCl)}{(HOCl) + (OCl^-)} = \frac{1}{1 + \dfrac{(OCl^-)}{(HOCl)}} = \frac{1}{1 + \dfrac{K_i}{(H^+)}} \qquad (4\text{-}9)$$

Example: At 20°C and pH 8, the percent distribution of HOCl is:

$$100 \times \left[1 + \frac{2.61 \times 10^{-8}}{10^{-8}}\right]^{-1} = \frac{100}{3.61} = 27.65\%$$

## Effect of Ionic Strength (*I*)

The concentration of positive and negative ions in solution affects the ability of molecules to dissociate into their respective ions. In the case of HOCl, it is the $H^+$ ion and the $OCl^-$ ion. There is a powerful mutual attraction of oppositely charged ions, therefore the more ions (the more TDS) the stronger the forces are for the dissociation of the molecules. The more ions, the more TDS, the greater the ionic strength ±. Figure 13 in the Appendix illustrates the HOCl dissociation curve for three ionic strengths with water at 25°C. Examination of this curve shows 50 percent HOCl at $p$H 7.5 for $I = 0.001$. The TDS at this ionic strength is 40 mg/liter. At the same pH but in a water with an ionic strength of $I = 0.01$ (TDS = 400 mg/l) the HOCl concentration drops to 45 percent. Waters with a TDS concentration of 40 mg/l would be those obtained from melting snow packs. Those with very high TDS concentrations are to be found in many groundwa-

TABLE 4-3 HOCl Ionization Constant

| *Temperature (°C)* | *0* | *5* | *10* | *15* | *20* | *25* | *30* |
|---|---|---|---|---|---|---|---|
| $K_i \times 10^{-8}$ (moles /liter) | 1.488 | 1.753 | 2.032 | 2.320 | 2.621 | 2.898 | 3.175 |

Table 4-4[a]

| | Percent HOCl | | | | | | |
|---|---|---|---|---|---|---|---|
| pH | 0°C | 5°C | 10°C | 15°C | 20°C | 25°C | 30°C |
| 5.0 | 99.85 | 99.82 | 99.80 | 99.79 | 99.74 | 99.71 | 99.68 |
| 5.5 | 99.53 | 99.45 | 99.36 | 99.27 | 99.18 | 99.09 | 99.00 |
| 6.0 | 98.53 | 98.28 | 98.00 | 97.73 | 97.45 | 97.18 | 96.92 |
| 6.1 | 98.16 | 97.84 | 97.50 | 97.16 | 96.82 | 96.48 | 96.15 |
| 6.2 | 97.69 | 97.29 | 96.88 | 96.45 | 96.02 | 95.60 | 95.20 |
| 6.3 | 97.11 | 96.62 | 96.10 | 95.57 | 95.05 | 94.53 | 94.04 |
| 6.4 | 96.39 | 95.78 | 95.14 | 94.49 | 93.84 | 93.21 | 92.61 |
| 6.5 | 95.50 | 94.75 | 93.96 | 93.16 | 92.37 | 91.60 | 90.87 |
| 6.6 | 94.40 | 93.47 | 92.51 | 91.54 | 90.58 | 89.65 | 88.78 |
| 6.7 | 93.05 | 91.92 | 90.75 | 89.58 | 88.43 | 87.32 | 86.27 |
| 6.8 | 91.41 | 90.03 | 88.63 | 87.23 | 85.85 | 84.54 | 83.31 |
| 6.9 | 89.42 | 87.77 | 86.10 | 84.43 | 82.82 | 81.29 | 79.86 |
| 7.0 | 87.04 | 85.08 | 83.10 | 81.16 | 79.29 | 77.53 | 75.90 |
| 7.1 | 84.22 | 81.92 | 79.63 | 77.39 | 75.26 | 73.27 | 71.44 |
| 7.2 | 80.91 | 78.25 | 75.64 | 73.11 | 70.73 | 68.52 | 66.52 |
| 7.3 | 77.10 | 74.08 | 71.15 | 68.35 | 65.75 | 63.36 | 61.22 |
| 7.4 | 72.78 | 69.42 | 66.20 | 63.18 | 60.39 | 57.87 | 55.63 |
| 7.5 | 67.99 | 64.33 | 60.88 | 57.68 | 54.77 | 52.18 | 49.90 |
| 7.6 | 62.79 | 58.89 | 55.27 | 51.98 | 49.03 | 46.43 | 44.17 |
| 7.7 | 57.27 | 53.23 | 49.54 | 46.23 | 43.32 | 40.77 | 38.59 |
| 7.8 | 51.57 | 47.48 | 43.81 | 40.58 | 37.77 | 35.35 | 33.30 |
| 7.9 | 45.82 | 41.79 | 38.25 | 35.17 | 32.53 | 30.28 | 28.39 |
| 8.0 | 40.18 | 36.32 | 32.98 | 30.12 | 27.69 | 25.65 | 23.95 |
| 8.1 | 34.79 | 31.18 | 28.10 | 25.50 | 23.32 | 21.51 | 20.01 |
| 8.2 | 29.77 | 26.46 | 23.69 | 21.38 | 19.46 | 17.88 | 16.58 |
| 8.3 | 25.19 | 22.23 | 19.78 | 17.76 | 16.10 | 14.74 | 13.63 |
| 8.4 | 21.10 | 18.50 | 16.38 | 14.64 | 13.23 | 12.07 | 11.14 |
| 8.5 | 17.52 | 15.28 | 13.46 | 11.99 | 10.80 | 9.84 | 9.06 |
| 8.6 | 14.44 | 12.53 | 11.00 | 9.77 | 8.77 | 7.97 | 7.33 |
| 8.7 | 11.82 | 10.22 | 8.94 | 7.92 | 7.10 | 6.44 | 5.91 |
| 8.8 | 9.62 | 8.29 | 7.23 | 6,39 | 5.72 | 5.18 | 4.75 |
| 8.9 | 7.80 | 6.70 | 5.83 | 5.15 | 4.60 | 4.16 | 3.81 |
| 9.0 | 6.29 | 5.39 | 4.69 | 4.13 | 3.69 | 3.33 | 3.05 |
| 9.5 | 2.08 | 1.77 | 1.53 | 1.34 | 1.19 | 1.08 | 0.98 |
| 10.0 | 0.67 | 0.57 | 0.49 | 0.43 | 0.38 | 0.34 | 0.31 |
| 10.5 | 0.21 | 0.18 | 0.15 | 0.14 | 0.12 | 0.11 | 0.10 |
| 11.0 | 0.07 | 0.06 | 0.05 | 0.04 | 0.04 | 0.03 | 0.03 |
| 11.5 | 0.02 | 0.02 | 0.015 | 0.013 | 0.012 | 0.01 | 0.01 |
| 11.7 | 0.01 | 0.01 | 0.01 | 0.01 | 0.007 | 0.007 | 0.006 |

[a] Computer printout *courtesy* D. S. Cherry, N.C. State Univ., Raleigh, N.C.

ters and some surface waters. Those with the highest TDS concentration; i.e., greater than 400 mg/l, would probably be highly polished reclaimed wastewater effluents.

The ionic strength of any solution can be calculated from a known TDS concentration by use of the following equation:

$$K_i = \frac{[f_{H^+})(H^+)][(f_{OCl^-})(OCl^-)]}{(HOCl)} \qquad (4\text{-}9a)$$

where $f$ is the activity coefficient of the ionic species, $H^+$, and $OCl^-$, and $K_i$ is the ionization constant. For very dilute solutions (TDS 10 mg/l) $f = 1.0$. So as $I$ approaches zero, $f$ approaches unity.

To determine the ionic strength of a particular water, the activity coefficients have to be determined. These can be approximated by the Debye–Hückel equation. This equation and the appropriate constant needed to solve this equation are to be found in the Appendix.

## Hypochlorite Solutions

The exact same chemical reaction occurs when hypochlorite solutions are used instead of aqueous chlorine solutions. If, for example, common bleach (sodium hypochlorite) is used it disperses in water to form hypochlorous acid:

$$NaOCl + H_2O \longrightarrow HOCl + NaOH \qquad (4\text{-}10)$$

The hypochlorous acid formed by this reaction proceeds to dissociate as in Eq. (4-6).

Familiarity with these factors is essential to an understanding of the behavior of dilute chlorine solutions, because HOCl and $OCl^-$ ion have very different germicidal efficiencies, as will be discussed later in this chapter.

To properly understand the chemistry of the basic reaction of chlorine in an aqueous solution, Eq. (4-1), it is helpful to understand the structure of the chlorine atom.

Chlorine has the periodic number 17, which indicates that there are seventeen positively charged protons in the nucleus of the chlorine atom. These protons in the nucleus are neutralized by seventeen negatively charged electrons in a series of outer shells. Two of the outer shells contain an irrevocable number of electrons, two in the first and eight in the second. These electrons are not available for reaction. This, then, leaves seven electrons of a possible eight in the last outer shell. Since this shell lacks one electron, it is not closed. This means that there are seven electrons available for reaction. If the chlorine atom were to lose these seven electrons in a chemical reaction, the atom would then have an excess of seven positive protons, giving the chlorine atoms a valence of +7. Furthermore, the nature of the chlorine atom is such that this outer open shell can take on a maximum of only eight electrons in its outer shell to give one negative electron in excess over the protons; this results in a valence of −1 on the chlorine atom. When this situation of −1 valence occurs, the outer shell of the chlorine atom is filled to its maximum of eight electrons, thus giving a stable chlorine radical $Cl^{-1}$, which is recognized as the chloride radical.

## Valence of Chlorine

Example of the various valences of the chlorine atom in different compounds are as follows:

| | |
|---|---|
| Sodium perchlorate | $Na^{+1}\ Cl^{+7}\ O_4^{-8}$ |
| Sodium chlorate | $Na^{+1}\ Cl^{+5}\ O_2^{-6}$ |
| Chlorine dioxide | $Cl^{+4}\ O_2^{-4}$ |
| Sodium hypochlorite | $Na^{+1}\ O_2^{-2}\ Cl^{+1}$ |
| Hypochlorous acid | $H^{+1}\ O^{-2}\ Cl^{+1}$ |
| Hydrochloric acid | $H^{+1}\ Cl^{-1}$ |
| Monochloramine | $N^{-3}\ H_2^{+2}\ Cl_2^{+1}$ |
| Dichloramine | $N^{-3}\ H^{+1}\ Cl_2^{+2}$ |
| Nitrogen trichloride | $N^{-3}\ Cl_3^{+3}$ |

Therefore the chlorine atom can have a valence ranging from +7 to −1.

Next, we see that all molecules and compounds must have a sum valence of zero, which means that all of the electrons are balanced by the protons. The chlorine molecule can therefore be considered as two chlorine atoms, $Cl^{+1}Cl^{-1}$, each having a positive and a negative valence balancing to zero. When the chlorine molecule becomes completely oxidized to two $Cl^{-1}$ ions, each with a valence of −1, only the positive chlorine atom of the molecule has undergone a change. It changes from valence +1 to valence −1, gaining two electrons for the chlorine molecule. Thus, chlorine is by definition an oxidizing agent. The rule is as follows: Any radical that loses electrons is being oxidized and is therefore a reducing agent. Conversely, any radical that gains electrons is being reduced and is an oxidizing agent.

When chlorine reacts with water, a special type of oxidation-reduction reaction takes place. The chlorine molecule with the sum valence of zero enters into what is known as a disproportionation reaction with water to form HOCl with a $Cl^{+1}$ radical and HCl with a $Cl^{-1}$ radical.[6] The sum valence of the reaction

$$Cl_2 + H_2O \longrightarrow H^{+1}O^{-2}Cl^{+1} + H^{+1}Cl^{-1} \qquad (4\text{-}11)$$

is still zero, indicating that no electrons have been gained or lost, thus signifying that no oxidation or reduction has occurred and that no available chlorine has been lost in forming HOCl. Now, when oxidation of a substance by HOCl takes place, the $Cl^{+1}$ radical in the hypochlorous acid will steal two electrons from the substance being oxidized and will then become a chloride radical with a valence of −1. This gain of two electrons by definition shows that the oxidizing capacity of the HOCl is equal to two equivalents of chlorine or one mol of $Cl_2$.

$$H^+ + Cl^- + HOCl + 2e^- \longrightarrow H_2O + 2Cl^- \qquad (4\text{-}12)$$

## Available Chlorine

The term "available chlorine" has no place in the field of water and waste treatment. This term was established as the basis for comparing the potential bleaching or disinfecting power of chlorine compounds. To compare one bleaching compound with another, it was necessary to be able to establish the oxidizing power of any such compound. This had to be accomplished by a quantitative analysis of the chlorine that was available for oxidizing, or, as seen above, how much chlorine with a valence of greater than −1 is present in the compound. At that time, the only quantitative method in use was the starch-iodide test, now known as the iodometric method.[7] When potassium iodide is added to a solution containing chlorine available for an oxidizing reaction, it will liberate iodine quantitatively from the potassium iodide, as follows:
Hypochlorous Acid:

$$HOCl^{+1} + 2KI^{-2} + HAc^* = I_2^0 + KCl^{-1} + KAc + H_2O \qquad (4\text{-}13)$$

Sodium Hypochlorite:

$$NaOCl^{+1} + 2KI^{-2} + 2HAc = I_2^0 + NaCl^{-1} + 2KAc + 2H_2O \qquad (4\text{-}14)$$

Monochloramine:

$$NH_2Cl^{+1} + 2KI^{-2} + 2Hac = I_2^0 + KCl^{-1} + KAc + NH_4Ac \qquad (4\text{-}15)$$

Dichloramine:

$$NHCl_2^{+2} + 4KI^{-4} + 3HAc = 2I_2^0 + 2KCl^{-1} + 2KAc + NH_4Ac \qquad (4\text{-}16)$$

From the foregoing basic chemistry, two things are evident: (1) Each chlorine radical with a valence of +1 will liberate elemental iodine $I_2$ on a quantitative basis; and (2) since all of the chlorine compounds (those that contain at least

---

Ac = acetic acid

one chlorine radical with ±1 valence) are made from elemental chlorine $Cl_2$, it really takes one molecule of $Cl_2$ to liberate one molecule of $I_2$.

To show how the available chlorine percentage is determined, let us examine the case of sodium hypochlorite (NaOCl):

$$\begin{array}{llll} \text{Na} & \text{O} & \text{Cl} & \text{mol wt} = 74.5 \\ 23 & 16 & 35.5 & = 74.5 \end{array}$$

$$\text{available chlorine (by wt)} = \frac{35.5}{74.5} = 47.7\%$$

In Table 4-5, multiply the percent by weight of chlorine actually present by 2, to give 95.4 percent available chlorine. This shows that the term "available chlorine" is a misnomer, as it is the calculated weight of elemental chlorine ($Cl_2$) that is required to liberate the same amount of elemental iodine. Since only half of the elemental chlorine molecule is of positive valence, when in solution, the available chlorine content of any chlorine compound which has a $Cl^+$ radical will always be twice the amount of this radical present.

Further proof of this lies in the manufacture of hypochlorite. For example, 10 percent by wt of active chlorine in a sodium hypochlorite solution contains 0.834 lb of active chlorine per gallon. This means that the manufacturer had to use 0.834 lb of chlorine gas (elemental chlorine, $Cl_2$) to make every gallon of the solution. Furthermore, if ten gallons of this solution were required to give a 0.5 ppm chlorine residual to one million gallons of water treated, it would simply

**Table 4-5 Available Chlorine**

| *Compound* | *Mol wt.* | *Mol of Equivalent* Chlorine* | *Percent of Chlorine by Weight* | |
|---|---|---|---|---|
| | | | *Actually Present* | *Available* |
| $Cl_2$ | 71 | 1 | 100 | 100 |
| HOCl | 52.5 | 1 | 67.7 | 135.4 |
| NaOCl | 74.5 | 1 | 47.7 | 95.4 |
| $Ca(OCl)_2$ | 143 | 2 | 49.6 | 99.2 |
| $NH_2Cl$ | 51.5 | 1 | 69.0 | 138.0 |
| $NHCl_2$ | 86 | 2 | 82.5 | 165.0 |
| $NCl_3$ | 120.5 | 3 | 88.5 | 265.5 |

* Number of mol of chlorine having an oxidizing capacity equivalent to one mol of the compound.

require 8.34 lb of chlorine gas dissolved in one million gallons of water to produce the same residual.

In summary, the term "available chlorine" is a misnomer. Actually, it refers to the oxidizing power of the compound tested, and is always twice the value of the active chlorine by weight present in that compound. The term "available chlorine" is analogous to alkalinity as "calcium carbonate." There could even be a case of a compound being tested which does not contain any chlorine at all. For example, it is proper to use the term "available chlorine" when comparing the oxidizing power of ozone. The reader is cautioned that this term is not be confused with the term "free available chlorine," which is the concentration of hypochlorous acid and hypochlorite ions existing in chlorinated water.

## Chlorine and Nitrogenous Compounds

The most important and undoubtedly the most complex chemistry of water and wastewater chlorination is its reaction with various forms of nitrogen naturally occurring in water

If the water to be treated did not contain nitrogenous compounds, the chlorination of water would be extremely simple. The total residual would always be free available chlorine. There would be no problem with quantitative determination of residuals. The disinfecting efficiency of chlorine could be predicted and controlled within a negligible margin of error. Problems of taste and odor from chlorination would probably be nonexistent.

However, this is not the case. Nitrogen appears in most natural waters and in varying amounts as either organic or inorganic nitrogen. These compounds of nitrogen and their relationship to chlorination will be considered in the general grouping as follows:

| *Inorganic Nitrogen* | *Organic Nitrogen* |
|---|---|
| Ammonia | Amino Acids |
| Nitrites | Proteins |
| Nitrates | |

The chemical stae of any nitrogen compound found in nature is a function of time in the overall life processes of all plants and animals. The amounts of these various forms of nitrogen relate directly to the sanitary quality of the water to be treated. These compounds fit very definitely in time on the nitrogen cycle of nature's own processes of purification. A look at the nitrogen cycle (Fig. 4-1) will show the relationship which exists between the various nitrogen compounds and the changes that are likely to occur in nature.[8] Consider the nitrogen cycle as a clock. Organic nitrogen from plant protein occurs at, say, 6 A.M., while organic nitrogen from animal protein occurs at 8 A.M. The first appearance of inorganic

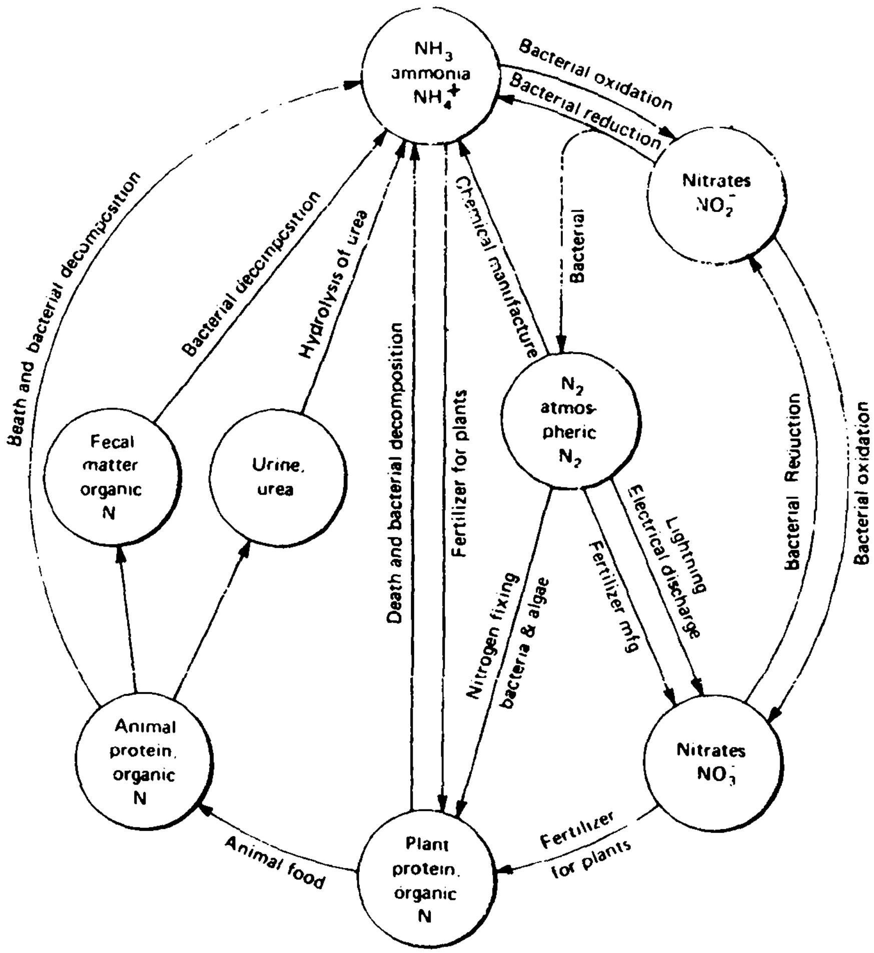

Fig 4-1 The Nitrogen cycle After Sawyer[8]

nitrogen in the form of ammonia occurs at Noon. The completion of the stabilization of the nitrogen compounds occurs at about 4 P.M. in the form of nitrates. These are then available to start the process all over again. This is obviously an oversimplification of the process. It is the relationship in time that is important. Further, it should be remembered that nitrogen and its compounds are in a continuous state of flux throughout this cycle. The various reactions are continuously competing with one another. Nature has conveniently set up a stored supply of nitrogen in the atmosphere, which can reach the earth's surface in two ways. One is by electrical discharge during a storm. In this case, the nitrogen is converted to $N_2O_5$, which hydrolyzes on contact with water to $HNO_3$, and falls to earth in solution with

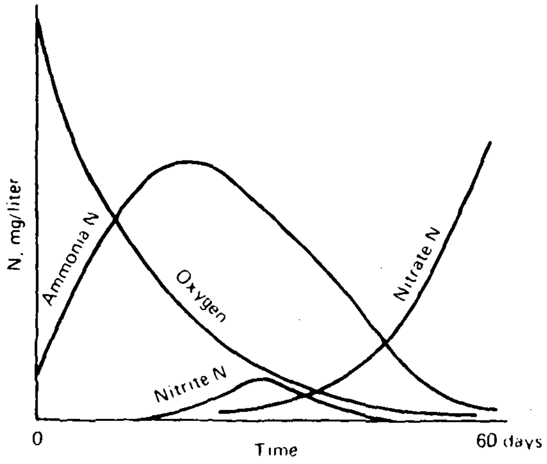

Fig. 4-2. Relationship of nitrogen compounds occurring in polluted water under aerobic conditions. After Sawyer.[8]

the rain. The second way is by nitrogen-fixing bacteria and algae which have the ability to extract nitrogen directly from the atmosphere.

Certain conclusions can be drawn about the degree of pollution of water if the chemical composition of the nitrogen compound is known. For example, it is safe to say: that water containing only nitrates is rather remote in time from any pollution; that water containing nitrites will be highly suspicious; and that waters containing mostly organic nitrogen and ammonia will have been subjected to recent pollution. However, the nitrogen method of pollution evaluation is not sensitive enough to predict whether a polluted body of water constitutes a public health hazard. The general relationship of these compounds occurring in polluted water undergoing purification by aerobic processes is best illustrated in Fig. 4-2.

The reaction of chlorine with any compound containing the nitrogen atom with one or more hydrogen atoms attached will form a compound broadly classified as an N-chloro compound, or, more commonly, as chloramine. There are two distinct classes of chloramines—organic, and inorganic. The inorganic chloramines are formed by the reaction of chlorine in an aqueous solution with free ammonia naturally occurring in the potable water or wastewater being treated. These chloramines are relatively simple compounds.

## THE BREAKPOINT PHENOMENON

### Introduction

The chemistry of this phenomenon is based upon the inorganic reaction of chlorine with ammonia nitrogen In dilute aqueous solutions (1-50 mg/l) the reaction between ammonia nitrogen and chlorine forms three types of chloramines in the following competing reactions:

$$HOCl + NH_3 \longrightarrow NH_2Cl \text{ (monochloramine)} + H_2O \qquad (4\text{-}17)$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 \text{ (dichloramine)} + H_2O \qquad (4\text{-}18)$$

$$NH_2Cl + HOCl \longrightarrow NCl_3 \text{ (trichloramine*)} + H_2O \qquad (4\text{-}19)$$

These reactions are in general by steps, so that they all compete with each other. A series of complex reactions with all of these substances involves the chlorine substitution of each of the hydrogen atoms in the ammonia molecule. These competing reactions are grossly dependent upon $p$H, temperature, contact time, initial chlorine to ammonia ratio, and most of all upon the initial concentrations of chlorine and ammonia nitrogen. Note that in all three equations the chlorine atom is positively charged.

The reaction of Eq. 4-17 will convert all of the free chlorine to monochloramine at pH 7 to 8 when the ratio of chlorine to ammonia is equimolar (5:1 by wt) or less—that is, 4:1, 3:1, and so on.

The rate of this reaction Eq. (4-17) is extremely important, since it is pH-sensitive. According to reaction rates established by Morris,[9,10] the fastest conversion of HOCl to $NH_2Cl$ occurs at pH 8.3. The following are calculated reaction rates for 99 percent conversion of free chlorine to monochloramine at 25°C with a molar ratio of $0.2 \times 10^{-3}$ mol/l HOCl and $1.0 \times 10^{-3}$ mol/l $NH_3$:

| *pH* | *seconds* |
|---|---|
| 2 | 421 |
| 4 | 147 |
| 7 | 0.2 |
| 8.3 | 0.069 |
| 12 | 33.2 |

The reaction slows appreciably as the temperature drops. At 0°C, it requires nearly five minutes for 90 percent conversion at pH 7.

The pH dependence of this reaction is described accurately on the basis of the $HOCl - OCl^-$ equilibrium and the $NH_3 - NH_4^+$ equilibrium.

The reaction of Eq. (4-18) will form dichloramine between pH 7 and 8 if the ratio of chlorine to ammonia is 2 mol chlorine to one mol ammonia nitrogen (10:1 by wt). The rate of this reaction is much slower than that of Eq. 4-17. It may take as long as one hour for 90 percent conversion[9] and up to five hours at pH 8.5 and above when ammonia nitrogen concentrations are very low. As the pH approaches 5 the reaction speeds up appreciably. This reaction is dependent on pH, initial ammonia nitrogen, and temperature. The reaction time of Eq. (4-18) is known to be minutes when the initial nitrogen concentration is in excess of 1 mg/l and the pH is favorable.

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* More commonly called nitrogen trichloride

The reaction of Eq. (4-19) will form some nitrogen trichloride when the pH is between 7 and 8 if the chlorine to ammonia nitrogen ratio is 3 mol of chlorine to 1 mol of ammonia nitrogen (15 : 1 by wt). At present very little is known about the kinetics of this reaction, particularly in concentrations of less than 10 ppm ($10^{-4}$ *M*). Nitrogen trichloride does form, even at equimolar ratios of chlorine to ammonia nitrogen, if the pH is depressed to 5 or less. At one time it was thought that it would not form above pH 5. It is known to exist in water treatment plants when the pH is as high as 9.[11] This occurs at very high chlorine to ammonia nitrogen ratios (25 : 1 by wt).

In waterworks practice, if the chemistry of Eq. (4-17) is practiced, it is known as either the chlorine-ammonia process, the chloramine process or chloramination. Eqs. (4-18) and (4-19) are related to the "breakpoint" phenomenon. It was Griffin's work which led to the discovery of this phenomenon in 1939.[12,13] Griffin was attempting to explain the sudden loss of chlorine residuals and the simultaneous disappearance of ammonia nitrogen at treatment plants which were experimenting with higher than usual chlorine residuals (2–15 mg/l).

These high residuals were used in an attempt to destroy obnoxious taste and odors. Griffin was startled to find that increasing the chlorine dose in certain waters not only did not increase the residual but reduced it significantly. He called this point of maximum reduction of residual the breakpoint. Fig. 4-3 illustrates this phenomenon, with point *A* designated as the breakpoint.

The importance of the breakpoint phenomenon is its relationship to the control of taste and odors either naturally present in the water or caused by the addition of chlorine. Griffin found that tastes and odors occurring in the region on the left of *A* disappeared on the right of *A* in Fig. 4-3. Other significant benefits were experienced in plant practice, the most important being the increased germicidal efficiency. The killing power of chlorine on the right of *A* is 25-fold or more than on the left of *A*.

Attempts to explain Griffin's findings[13,14] led to serious scientific investigations between 1946 and 1950. The most extensive laboratory investigation was accomplished at Harvard University. The work of Fair, Morris, Chang, Weil, Burden, Culver, and Granstrom is largely responsible for our present knowledge of the physical chemistry of chlorination.[9,15-22] Palin's work in England during the same period is also noteworthy.[23,24] Williams' work on a plant scale substantiates the findings of both Palin and the Harvard group.[25-27] Williams' work is of significant importance because it documents a period of 20 years and because it demonstrates the practical value of this knowledge. It is of historical interest to note that all of these investigations substantiated that of Holwerda done almost 20 years earlier.[28] The work at Harvard was an effort directed primarily toward the explanation of the mechanism that triggers the breakpoint. These investigators used the most sophisticated and accurate method available for the identification of the various chlorine residual fractions—namely, the light absorbance principle of the spectrophotometer

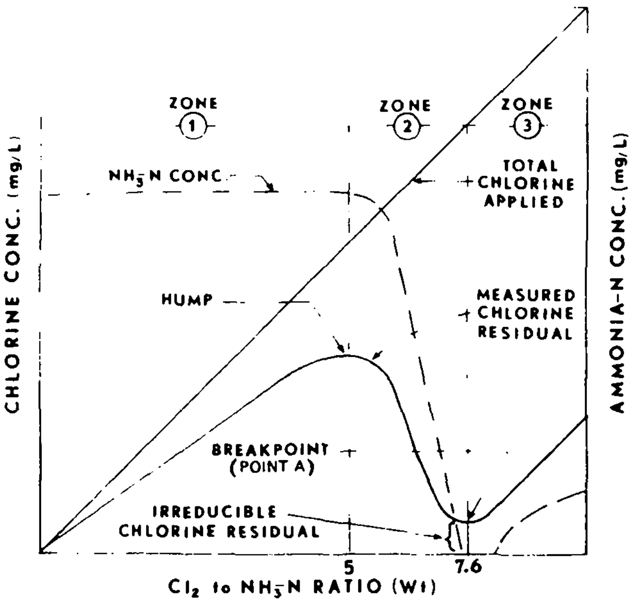

Fig. 4-3. Theoretical breakpoint curve.

## The Breakpoint Curve

The breakpoint curve is a graphic representation of chemical relationships which exist as varying amounts of chlorine are added to waters containing small amounts of ammonia nitrogen. The theoretical breakpoint curve is shown in Fig. 4-3. It was originally developed as a result of Griffin's work in 1941–44.[13,14] This curve has several characteristic features. The principal reaction in Zone 1 is the reaction between chlorine and the ammonium ion indicated in Eq. (4-17). This results in a chlorine residual containing only monochloramine all the way to the hump in the curve. The hump occurs, theoretically, at a chlorine to ammonia nitrogen weight ratio of 5 : 1 (molar ratio of 1 : 1). This ratio indicates the point where the reacting chlorine and ammonia nitrogen molecules are present in solution in equal numbers. As the molar ratio begins to exceed 1 : 1 some of the monochloramine starts a disproportionation reaction* to form dichloramine in accordance with Eq. (4-18).[22]

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* A disproportionation reaction is one that transforms a substance into two dissimilar compounds by a process involving simultaneous oxidation and reduction. Therefore the chemical equilibrium in Zone 2 favors the formation of dichloramine and the oxidation of ammonium ion according to Eqs. (4-17), (4-18), and (4-19). This results in a marked reduction of ammonia nitrogen caused by the oxidation of chlorine. The above reactions proceed in competition with each other to produce a breakpoint at a theoretical $Cl_2$ to $NH_4^+$ weight ratio of 7.6 to 1. At the breakpoint (Point A) ammonia nitrogen is either at a minimum or disappears entirely.

To the right of the breakpoint, Zone 3, chemical equilibria require the build-up of free chlorine residual (HOCl). In practical applications of breakpoint chlorination, reactions occur which result in the formation of nitrogen gas, nitrate, nitrogen trichloride, and other end products. These reactions consume chlorine and cause the $Cl_2:NH_4^+$ ratio to exceed the stoichiometric value of 7.6 : 1 and affect the shape of the breakpoint curve.†

As the chlorine to ammonia nitrogen ratio increases beyond about 12–15 : 1 the reaction of Eq. (4-19) sets in. Under these conditions the formation of nitrogen trichloride will occur even at *p*H values as high as 9. As the chlorine dose is increased beyond point *A* in Zone 3 the free available chlorine residual will increase in an amount equal to the increase in the dosage. Therefore, the breakpoint curve in Zone 3 should plot at a 45° angle.

It should be emphasized that the shape of the breakpoint curve is affected by contact time, temperature, concentration of chlorine and ammonia, and *p*H. High concentrations increase the speed of the reactions. As the *p*H decreases below 8.3 the reactions are retarded. The higher the temperature the faster the reactions. The shape of the curve is different for different contact times.

In potable water practice this is known as free residual chlorination rather than the breakpoint process. In potable water treatment the practical significance of the curve is briefly as follows:

*Zone 1.* The residuals in this zone up to the hump are all monochloramine. The residuals in this zone do not form trihalomethanes nor do they usually contribute to tastes and odors.

*Zone 2.* As the hump is passed the monochloramine plus the addition of more free chlorine begins to form dichloramine, which is about twice as germicidal as monochloramine. However, this may not be the best part of the curve for the production of a palatable water. A pure dichloramine residual has a noticeable disagreeable taste and odor, while monochloramine does not. It is generally considered best to avoid this part of the curve in order to avoid taste and odor problems.

*Zone 3.* At the dip of the curve (point A) and beyond, free chlorine residual will appear. The total residual will be made up of the nuisance residuals plus free chlorine. If nitrogen trichloride is formed it will appear in this zone. In practice it has been found that a ratio of free chlorine to total residual of 85 percent or greater will result in the most palatable water.

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† The following values have been observed at the breakpoint: Griffin and Chamberlin observed 10–12.5 : 1 at *p*H values between 6 and 9;[13] Palin observed 9.5 : 1 at *p*H 6, 8.25 : 1 at *p*H 7, and 8.4 : 1 at *p*H 9;[24] Moore, Megregian, and Ruchhoft observed an average value of 9.0 : 1 at *p*H 6–9;[24] Metropolitan Water District of Southern California has observed values of 9 : 1 at *p*H 7.9 and 11 : 1 at *p*H 7.5 in their two different supplies.[35] This is also the point at which there exists an irreducible minimum of chlorine residual commonly described as "nuisance residuals." These residuals titrate as predominantly dichloramine with a trace of free chlorine and monochloramine. Griffin also discovered that in Zone 3 there will be a return of ammonia nitrogen.

## The Breakpoint Reaction

The mechanism by which the breakpoint phenomenon occurs was first proposed by Rossum in 1943.[30] He calculated the distribution of mono- and dichloramine by means of mass action equations. Although he recognized the possible occurrence of nitrogen trichloride, he considered the breakpoint reaction as one of the relationships of mono- and dichloramine. He confirmed Griffin's finding that ammonia does reappear to the right of the dip in the curve, and was one of the first to observe the destruction of free chlorine (HOCl) by sunlight.

The equilibrium condition between mono- and dichloramine in equimolar concentrations was established by the Harvard group, using spectrophotometric methods.[31] This work demonstrated that the equilibrium condition between mono- and dichloramine can be expressed as follows:

$$\frac{(NH_4^+)\,(NHCl_2)}{(H^+)\,(NH_2Cl)^2} = 6.7 \times 10^5 = K_{eq} \qquad (4\text{-}20)$$

Curve *A* in Fig. 4-4 shows this equilibrium relationship for mono- and dichloramine at different *p*H levels based on Eq. (4-20).

The work of other investigators is also shown. It is interesting to note that Chapin's work[32] using a variation of the starch–iodide technique for the residual fractions compares more closely to the expression in Eq. (4-20) than do the others. However, Palin's[24] and Baker's[33] work tend to agree with each other. Palin separated the residual fractions by neutral O-T FAS titration. Baker used the amperometric titration method, as did Kelly and Sanderson.[34] For unknown reasons, the work of Kelly and Sanderson does not compare favorably with the rest. Williams' work,[36,37] which is on a plant operation, more nearly substantiates the Harvard investigation.

From all of this information, Morris[9] suggested that the key to the final breakpoint reaction was the formation and decomposition of dichloramine. This work, in turn, inspired the investigation of the disproportionation reaction of monochloramine in the breakpoint phenomenon.[21] This investigation has led to the following information about the breakpoint phenomenon:

As the chlorine to ammonia nitrogen ratio proceeds from 5:1 to 10:1 and greater, two important reactions take place which tend to shift the relative concentrations of mono- and dichloramine:

1 The spontaneous conversion of monochloramine forms dichloramine and ammonia. This is known as the disproportionation of monochloramine.
2 The decomposition of dichloramine decreases its concentration.
These two reactions are thought to occur only in the presence of excess free chlorine.

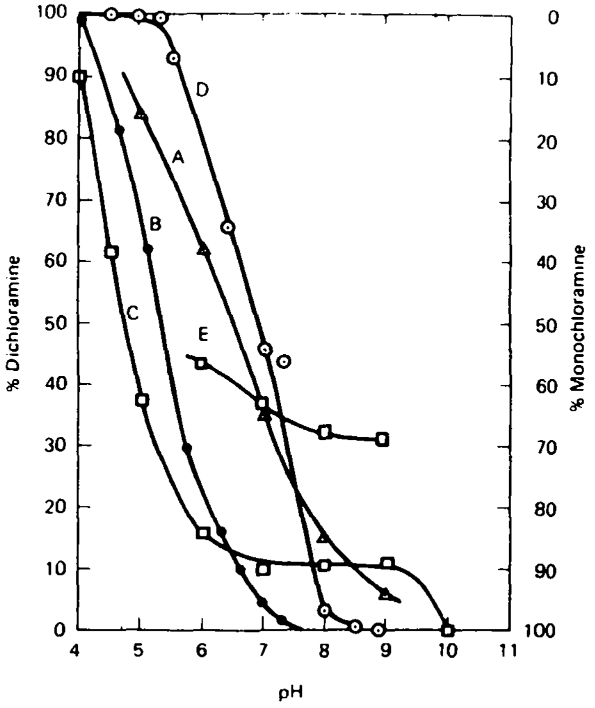

Fig. 4-4. Distribution of monochloramine and dichloramine with relation to pH. Curve A = Fair et al[31] $Cl-NH_3$ wt. ratio 5:1; curve B = Palin[24] $Cl-NH_3$ 5:1, 2 hr contact; curve C = Baker[33] $Cl-NH_3$ 4:1 2-hr contact; curve D = Chapin[32] (excess $NH_3$); curve E = Kelly and Sanderson,[34] $Cl-NH_3$ 2:1 (Curve A computed from EQ20, $K_{eq} = 6.7 \times 10^6$).

The conversion of mono- to dichloramine takes place by means of hydrolysis of a monochloramine molecule to form HOCl, which then reacts with another monochloramine molecule to form dichloramine as follows:

$$\begin{array}{l} NH_2Cl + H_2O \longrightarrow HOCl + NH_3 \\ \qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\quad NH_2Cl \longrightarrow NHCl_2 + H_2O \end{array} \tag{4-21}$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \tag{4-22}$$

This is considered to be a first-order reaction, which does not seem to be affected by the pH or the buffering of the solution.

There is also a second-order reaction, which proceeds in parallel with the previous one, but is pH- and buffer-dependent. It is thought to proceed by means of acid catalysis. This reaction probably occurs between a monochloramine acid complex catalyst, which then reacts with another monochloramine molecule to form dichloramine, as follows:

$$\begin{gathered} NH_2Cl + \text{Acid} \rightleftarrows [NH_2Cl \cdot \text{Acid}] \\ [NH_2Cl \cdot \text{Acid}] + NH_2Cl \rightleftarrows NHCl_2 + NH_3 + \text{Acid} \end{gathered} \qquad (4\text{-}23)$$

(In any catalytic reaction, the catalyst is never lost.)

These two reactions then make up the spontaneous conversion of mono- to dichloramine, known as the disproportionation of monochloramine.

While the rate of formation of monochloramine is dependent on the concentration of ammonia and free chlorine, it is dependent also on pH (because of the equilibria $H^+ + OCl^- \rightleftarrows HOCl$ and $NH_4 \rightleftarrows H^+ + NH_3^-$) but is not affected by the buffering of the solution, whereas the rate of formation of dichloramine is acid-catalyzed—in other words, it is dependent upon the buffering of the solution.

An excess of ammonia suppresses the disproportionation reaction of monochloramine. There must be an excess of HOCl for Eqs. (4-22) and (4-23) to proceed.

The next step in the breakpoint reaction is the decomposition of the dichloramine, which is dependent on the hydroxyl ion activity. Morris[9] has proposed the following mechanism for the decomposition of dichloramine:

First, the dichloramine ionizes as a weak acid:

$$NHCl_2 \longrightarrow H^+ + NCl_2^- \qquad (4\text{-}24)$$

This proceeds to react with the hydroxyl ion ($OH^-$) in either of two possible ways:

$$NCl_2^- \xrightarrow{(OH)} N - Cl + Cl^- \qquad \text{(slow) } (4\text{-}25)$$

$$N - Cl + OH^- \longrightarrow NOH + Cl^- \qquad \text{(fast) } (4\text{-}26)$$

or:

$$(NCl_2)^- + (OH)^- \longrightarrow NCl(OH)^- + Cl^- + H^+ \qquad (4\text{-}27)$$

$$NCl(OH)^- \longrightarrow NOH + Cl^- \qquad (4\text{-}28)$$

Eq. (4-28) shows the formation of an intermediate reaction product, the nitroxyl radical NOH. This can proceed to decompose into the end products of the reaction in three ways. Each way is valid since the end products depend on many variables, such as molar ratio of chlorine to ammonia, initial ammonia nitrogen concentration, pH, temperature, and unknown side reactions of chlorine and organic matter.

The first way assumes that the predominant end point of the breakpoint reaction might be $N_2O$ as first postulated by Chapin.[32] This would require the formation of hyponitrous acid from two nitroxyl radicals through dimerization:

$$2\ NOH \longrightarrow H_2N_2O_2 \tag{4-29}$$

The hyponitrous acid slowly decomposes to give nitrous oxide:

$$H_2N_2O_2 \longrightarrow N_2O + H_2O \tag{4-30}$$

This mechanism calls for two moles of chlorine for every atom of nitrogen that is oxidized. Morris[39] points out that Palin found that it required less than two moles of chlorine to oxidize each atom of nitrogen, which suggests the possibility that nitrogen gas ($N_2$) is the predominant end product. In view of this statement it is interesting to note that the recent work (1970) on nitrogen removal from wastewater by Pressley, Bishop, and Roan[40] concludes that it requires less than two moles of chlorine to oxidize one atom of nitrogen and that the end products of the reaction were found to be $N_2$, $NO_3^-$, and $NCl_3$.

The second way the breakpoint reaction might proceed would be to assume that the main end product is nitrogen gas ($N_2$). The decomposition of dichloramine to produce the intermediate reactive product NOH would be as follows:[39]

$$NHCl_2 + H_2O \longrightarrow NOH + 2H^+ + 2Cl^- \tag{4-31}$$

This would be followed by three competing reactions involving the intermediate, NOH, as follows:

$$NOH + NH_2Cl \longrightarrow N_2 + H_2O + H^+ + Cl^- \tag{4-32}$$

$$NOH + NHCl_2 \longrightarrow N_2 + HOCl + H^+ + Cl^- \tag{4-33}$$

$$NOH + 2\ HOCl \longrightarrow NO_3^- + 3H^+ + Cl^- \tag{4-34}$$

These hypothetical reactions are compatible with the end products of the breakpoint reaction.

Eq. (4-19) is a part of this reaction as it accounts for the formation of nitrogen trichloride ($NCl_3$) when an excess of chlorine is present. The reverse of this reaction:

$$NCl_3 + H_2O \longrightarrow NHCl_2 + HOCl \tag{4-35}$$

is required to demonstrate the well known fact that $NCl_3$ is quite stable under conditions of water chlorination only when an excess of chlorine is present, and to account for the slow decomposition of $NCL_3$. It is, however, easily aerated because of its low solubility in water.

The third breakpoint reaction could occur in the presence of a large excess of free chlorine.

$$H_2N_2O_2 + HOCl \longrightarrow 2NO + H_2O + H^+ + Cl^- \qquad (4\text{-}36)$$

This reaction would require 2.5 mol of chlorine for every nitrogen atom oxidized. This is what Griffin[13] found for large excesses of free chlorine in the pH range 6–9. (To convert ratios in moles to weight ratios multiply by 5, i.e., Cl : N = 71 : 14 = 5.)

It can be concluded then that the breakpoint phenomenon will occur when the ratio of chlorine to ammonia nitrogen by weight is from 9 to 1 or greater providing the *p*H of the environment is favorable. Reaction times are a function of initial ammonia nitrogen concentration but will range from minutes to hours for a given *p*H and temperature conditions. The optimum *p*H for the fastest reaction is between 7 and 8. Above and below this range the reaction slows appreciably. Lowering the temperature retards the reaction.

Other conclusions of academic interest may also be drawn. Free available chlorine is converted from its positive valence state to its negative valence, or chloride, state as a result of oxidizing the nitrogen atom. The end products are most probably released as gases of nitrogen compounds. If there is any carbonaceous material, chlorine will react with these compounds, with carbon exerting a chlorine demand and being released as carbon dioxide. This release of gases as a result of the breakpoint reaction is readily observed in rotameters installed in the chlorine solution lines. These rotameters are downstream from the injector and will carry a solution of HOCl at a concentration in the range of 500 to 3500 ppm. The pH is usually about 2. Copious quantities of gas bubbles are usually observed. Most of these bubbles will consist of $CO_2$ and be related to the alkalinity of the injector operating water. The nitrogen gases will be related to the amount of ammonia nitrogen present in the water. In treated wastewater, the organic nitrogen probably will not be released at this point, since the reaction time is not sufficient. A scientific investigation of this reaction might enhance our knowledge of chlorination chemistry. It might also serve to establish some design criteria, because the gas released in this phenomenon is sufficient to cause abnormal friction losses in solution lines and because in some waters the bubbles are of such magnitude that rotameters will not function.

Nitrites have been suggested as a possible product of decomposition. This is unlikely, since nitrites readily react with free chlorine and are oxidized rapidly to nitrates:[38]

$$NO_2^- + HOCl \longrightarrow NO_3^- + H^+ + Cl^- \qquad (4\text{-}37)$$

Nitrites will not react with chloramines in the pH range of 6 to 9. However, at *p*H 4 there is some indication of a reaction with dichloramine.

## Selleck-Saunier Breakpoint Chemistry

In an attempt to fully understand the chemistry of the breakpoint phenomenon, Prof. Selleck and graduate student Saunier decided to review this reaction using both potable water and wastewater. At the time there were disagreements in the literature concerning the chemical pathways to the end products. This work by Saunier[41,42] under the guidance of Prof. Robert E. Selleck, University of California, Berkeley, CA, resulted in the creation of a computer model based upon more than 80 experimental runs, within a *p*H range of 6–9; ammonia nitrogen from 1 to 20 mg/liter; and chlorine to nitrogen molar dose ratios of 1.6 : 3.5; and temperatures between 12°C and 21°C. The model as developed by this research can be used to compute the production of the various species of chlorine compounds formed during the breakpoint reaction; the *p*H of the water immediately after chlorine addition; the amount of chemical required for buffering the reaction to the optimum *p*H for the greatest speed of the reaction, as well as the decrease in *p*H as the reaction proceeds. Based on Saunier's[41] research the following set of reactions appears to be the most reasonable:[43]

$$NH_4^+ + HOCl \Rightarrow NH_2Cl + H_2O + H^+ \tag{4-38}$$

$$NH_2Cl + HOCl \Rightarrow NHCl_2 + H_2O \tag{4-39}$$

$$0.5\ NHCl_2 + 0.5\ H_2O \Rightarrow 0.5\ NOH + H^+ + Cl^- \tag{4-40}$$

$$0.5\ NHCl_2 + 0.5NOH \Rightarrow 0.5N_2 + 0.5\ HOCl + 0.5H^+ + 0.5\ Cl^- \tag{4-41}$$

and finally

$$NH_4^+ + 1.5\ HOCl \longrightarrow 0.5N_2 + 1.5\ H_2O + 2.5\ H^+ + 1.5\ Cl^- \tag{4-41a}$$

The above reactions are based on the formation of NOH, apparently a catalytic intermediary compound which Saunier and Selleck believe is a result of the formation of hydroxylamine ($NH_2OH$) as an intermediate reaction.[41,42] These reactions are as follows:

$$NHCl_2 + 2H_2O \longrightarrow NH_2OH + HCl + HOCl \tag{4-42}$$

$$NH_2OH + HOCl \longrightarrow NOH + HCl + H_2O \tag{4-43}$$

$$NOH + NHCl_2 \longrightarrow N_2 + HOCl + HCl \tag{4-44}$$

The formation of the hydroxylamine and the resulting formation of the catalytic compound NOH greatly increases the speed of the breakpoint reaction as the ammonia nitrogen concentration increases with the greater NOH production.

The breakpoint occurs through the sequential formation of monochloramine and dichloramine with the subsequent catalytic decomposition of dichloramine to produce an end product of nitrogen gas, with a partial return of free chlorine residual (HOCl) to the solution. These reactions confirm that 1.5 moles (gram molecular weight) of chlorine are required to oxidize 1.0 mole of ammonia to nitorgen gas.

Stoichiometrically, the breakpoint reaction requires a weight ratio of chlorine to ammonia nitrogen ($Cl_2:NH_4^+$-N) at the breakpoint of 7.6:1 as shown below:

$$\text{Molecular wt HOCl} = 70.9 \text{ (as } Cl_2)$$

$$\text{Moles HOCl required} = 1.5$$

$$\text{Molecular wt } NH_4^+ = 14 \quad \text{(as N)}$$

$$\text{Moles } NH_4^+ \text{ required} = 1.0$$

Therefore, $Cl_2 \cdot NH_4^+$-N = (1.5) (70.9):(1.0) (14.0) = 7.6:1; so for each mg per liter of $NH_4^+$-N, 7.6 mg per liter of chlorine is required to reach the breakpoint. In actual wastewater-treatment practice, as was demonstrated by the Rancho Cordova project, it required 10 mg per liter of chlorine for each 1.0 mg per liter ammonia nitrogen present in the process influent.[41] Approximately 70 percent of this breakpoint dosage was consumed to produce nitrogen gas ($N_2$) from the ammonium ion ($NH_4^+$) at pH set points between pH 7 and 8. The oxidation of $NH_4^+$ to $NO_3^-$ consumed 8 to 19 percent of the total chlorine dosed to the system. Overall, about 96 percent of the total chlorine dosage was accounted for in reactions between chlorine and nitrogeneous species in specific chemical pathways and free chlorine residual remaining in solution following breakpoint.

## Side Reactions of Breakpoint Chlorination

The following are some of the chemical reactions other than the direct oxidation of ammonia to nitrogen gas. The reaction products and chlorine consumption for such reactions are governed by factors such as the type and degree of pretreatment, initial $Cl_2:NH_4^+$-N ratio, pH, and alkalinity. These reactions are as follows:

| *Description* | *Reaction Stoichrometerity* | |
|---|---|---|
| Breakpoint reaction | $NH_4^+ + 1.5\,HOCl \longrightarrow 0.5N_2 + 1.5H_2O + 2.5H^+ + 1.5Cl^-$ | (4-45) |
| $NCl_3$ formation | $NH_4^+ + 3HOCl \longrightarrow NCl_3 + 3H_2O + H^+$ | (4-46) |
| Nitrate formation | | |
| 1-From ammonia | $NH_4^+ + 4HOCl \longrightarrow NO_3 + H_2O + 6H^+ + 4Cl$ | (4-47) |
| 2-From nitrite | $NO_2 + HOCl \longrightarrow NO_3 + H^+ + Cl^-$ | (4-48) |

## *p*H and Alkalinity Considerations

The nature and concentration of the breakpoint chlorination end products, the chlorine dosage required to reach breakpoint, and the rate of the breakpoint reaction are all affected by the initial *p*H (following chemical addition) and the *p*H change which occurs as the breakpoint reaction proceeds. The initial *p*H in the reaction zone and *p*H change through breakpoint depends upon the *p*H and alkalinity of the process influent stream, the ammonia concentration, the chlorine dosage, and the amount of alkalinity supplementation.

Acidity is generated in breakpoint chlorination applications (nitrogen removal) from both the hydrolysis and dissociation of chlorine gas (when $Cl_2$ gas solutions are used), and the oxidation of ammonia nitrogen.

When the acidity generated is from the hydrolysis and dissociation of chlorine gas the following reaction occurs:

$$1.5\ Cl_2 + 1.5\ H_2O \longrightarrow 1.50\ OCl^- + 3H^+ + 1.5\ Cl^- \qquad (4\text{-}49)$$

If acidity is from the oxidation of ammonia the following two reactions prevail:

$$NH_4^+ + 1.5\ OCl^- \longrightarrow 0.5\ N_2 + 1.5\ H_2O + H^+ + 1.5\ Cl^- \qquad (4\text{-}50)$$

and

$$NH_4^+ + 1.5Cl_2 \longrightarrow 0.5\ N_2 + 4\ H^+ + 3Cl^- \qquad (4\text{-}51)$$

To counteract the acidity generated in the above reactions either lime or caustic can be used as follows:

$$\textit{Lime: } 2\ CaO + H_2O \longrightarrow 2Ca^{++} + 4OH^- \qquad (4\text{-}52)$$

$$\textit{Caustic: } 4\ NaOH \longrightarrow 4Na^+ + 4OH^- \qquad (4\text{-}53)$$

Stoichiometrically, three moles of hydrogen ions are liberated in the hydrolysis and dissociation of chlorine gas to provide sufficient chlorine for the oxidation of one mole of ammonia nitrogen; assuming the initial *p*H in the reaction zone is alkaline. One mole of hydrogen ion is liberated in the oxidation of ammonia to nitrogen gas.

## Saunier's Research

Saunier studied the kinetics of the breakpoint reaction in both tap water and tertiary effluent.[41] Only the facets of this research will be discussed here as they may relate to tertiary effluents.*

One of the most important findings by Saunier was the confirmation that there

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* This includes water for reuse.

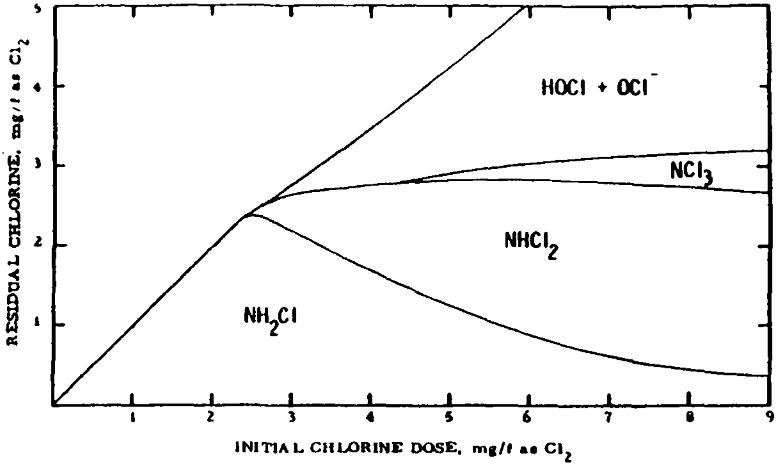

Fig. 4-5. Chlorine dose residual curves predicted by the model after 2.5 min. contact time (pH = 7.4, $NH_3$–N = 0.5 mg/liter, Temp = 15°C).

is a considerable time difference required to complete the breakpoint reaction as related to the ammonia nitrogen concentration, other factors being equal.

Fig. 4-5 illustrates the distribution of the chlorine residual species (as predicted by Saunier's model) when the $NH_3$-N is 0.5 mg per liter and the contact time is 2.5 min.; Fig. 4-6 is the same situation except that the contact time is 20 min. Fig. 4-7 is the predicted breakpoint kinetics but with an ammonia nitrogen concentration of 2.5 mg per liter.

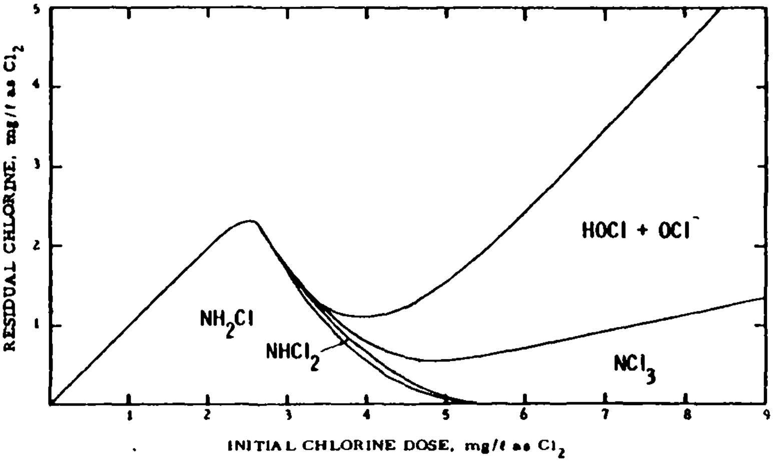

Fig. 4-6. Chlorine dose residual curves predicted by the model after 20 min. contact time (pH = 7.4 $NH_3$–N = 0.5 mg/liter, Temp = 15°C).

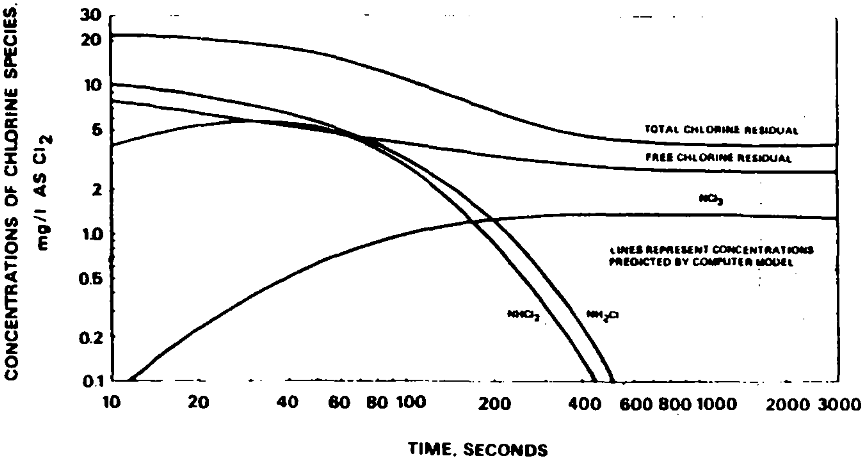

Fig. 4-7. Predicted breakpoint kinetics in a plug flow reactor (pH = 7.5, $NH_3$–N = 2.5 mg/liter, Temp = 15°C and $Cl_2/N$ = 9.0 by wt). The lines represent concentrations predicted by the model.

Compare these curves with Fig. 4-8 which is a tertiary effluent with an $NH_3$ -N content of 18 mg/liter and molar ratio of Cl:N of 1.77. The breakpoint reaction in Fig. 4-8 occurs in less than 3 min. (at the disappearance of $NH_2Cl$) while it takes about 20 min. for water containing less than 1.0 mg per liter $NH_3$ -N and about 8–10 min. when the $NH_3$ -N concentration is 2.5 mg per liter, other factors such as *p*H and temperature being equal. The model prediction of Fig. 4-8 is in close agreement with the Rancho Cordova project findings[43] where molar ratios of $Cl_2$ -$NH_3$ -N of 2:1 produced the breakpoint reaction in 60–90 sec. at $NH_3$ -N initial concentrations of 15 to 20 mg per liter. So for tertiary effluents nitrified to $NH_3$ -N concentrations of less than 2 mg per liter, it will require 15–20 min. to complete the breakpoint reaction and produce a controllable, stable, free chlorine residual.

Further findings by Saunier showed that after the breakpoint is reached, the resulting *dichloramine fraction* of the *residual is nearly as germicidal as the free HOCl residual,* and furthermore the HOCl residual is 30 times more germicidal than the $OCl^-$ ion. These findings are indeed different from previous findings.

Nitrogen gas and nitrate are the final end products of the breakpoint reaction. Nitrogen trichloride* formed during the reaction decreases slowly with time. While $NCl_3$ does not appear to be an end product of the reaction, for all practical purposes it is an end product; because in the time frame of the process in practice, the remaining $NCl_3$ (at the end of the contact time) will revert to ammonia nitrogen after dechlorination.

Saunier also confirmed the speed of the breakpoint reaction to occur most rapidly

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* Nitrogen trichloride is a most effective germicide.

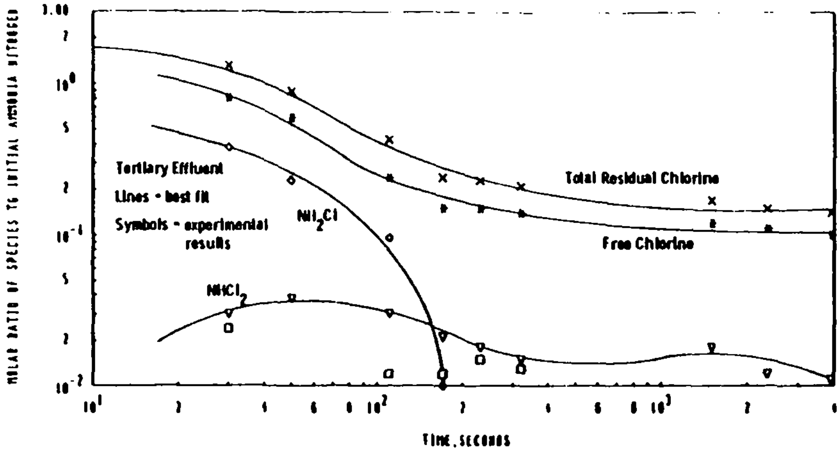


Fig. 4-8. Breakpoint chlorination kinetics of a tertiary effluent in a plug flow reactor (pilot plant experiment). pH = 7.50 after 150 sec., Temp. = 18.8°C, N = 18.03 mg/liter and $Cl_2/N$ = 1.77 molar ratio. Lines = best fit; symbols = experimental results.

at *p*H 7.5. He also confirmed that the $NCl_3$ concentration increased with increasing Cl to N ratios at all levels of *p*H. Also that the organochloramines interfered mainly with the dichloramine and indirectly with the $NCl_3$ DPD-FAS analysis, primarily at *p*H values above 7.5. Traces of organic nitrogen (0.02 mg per liter) formed organochloramines in sufficient amount to give false DPD-FAS dichloramine readings at *p*H values above *p*H 7.5. The oxidation of the organic nitrogen proceeded faster at *p*H values of less than 7.5.

In summarizing Saunier's findings, particularly as they relate to tertiary effluents, it can be concluded that if it is desired to achieve a free chlorine residual for bacteria and virus destruction, when the ammonia nitrogen concentration is less than 2.0 mg per liter, the process should be carried out at a control *p*H of 7.0–7.2 with a minimum contact period of 30 min. Moreover, Saunier's work shows some instability of the free chlorine residual in the usual control sampling time of 1 to 3 min. after the point of application. Therefore, residual control in situations where the initial ammonia nitrogen concentration is less than 2.0 mg per liter should be based on the total chlorine residual measurement.

At this level of chlorination with most wastewater effluents, *p*H adjustment due to the addition of chlorine would probably not be required. Most effluents have an alkalinity of 150 to 200 mg per liter which is easily capable of maintaining the *p*H at status quo with chlorine dosages as high as 25 mg per liter.

## Significance of Organic Nitrogen

Chlorination of waters containing organic nitrogen presents a variety of problems not encountered in waters containing ammonia nitrogen. Organic nitrogen looms as a formidable stumbling block in the production of an acceptable water, because of the complexity of the compounds that contain organic nitrogen

A little background on the source and nature of these compounds will be helpful in understanding the problem.

*Standard Methods*[7] gives analytical procedures for the determination of two nitrogen classifications that derive from other than ammonia nitrogen

1 One is albuminoid nitrogen, which gives only an approximation of the proteinaceous matter present in the water The nitrogen in this determination is thought to be related to the nitrogen content of the various amino acids

2. The other is total organic nitrogen, which is contributed in various degrees by proteins, polypeptides, and amino acids. In other words, the total organic nitrogen determination measures the nitrogen associated with proteins and all the hydrolytic products thereof

The proteins are the most difficult to deal with by chlorination Proteins are a constituent of plant and animal life normal to the aquatic life and are found in both human and animal waste. All proteins are made up of nitrogen, carbon, oxygen, and hydrogen, and some contain sulfur Of these elements nitrogen, carbon, and sulfur exert a chlorine demand. They are complex high molecular weight organic compounds found in various stages of hydrolysis. The hydrolysis is accomplished by hydrolytical enzymes, and the products of degradation are as follows:

$$\begin{tikzcd}
\text{protein} \arrow[r] & \text{proteoses} \arrow[r] & \text{peptones} \arrow[r] & \text{polypeptides} \arrow[d] \\
& \alpha\ \text{amino acids} & \text{dipeptides} \arrow[l] & \arrow[l, dashed]
\end{tikzcd}$$

The α amino acids are then deaminized by enzymic action, and free fatty acids and other acids result; the free acids serve as food for the microorganisms, which, in turn, are converted to carbon dioxide and water[8]

From the products of hydrolysis, we see that the proteins represent one end of the spectrum and the amino acids the opposite end. Therefore the chlorination of organic nitrogen compounds can be classified into these two categories. Likewise, the determination of loss of total organic nitrogen will represent the measure of oxidation of proteins by chlorine, while the loss of albuminoid nitrogen will measure the oxidation or decomposition of the amino acids involved.

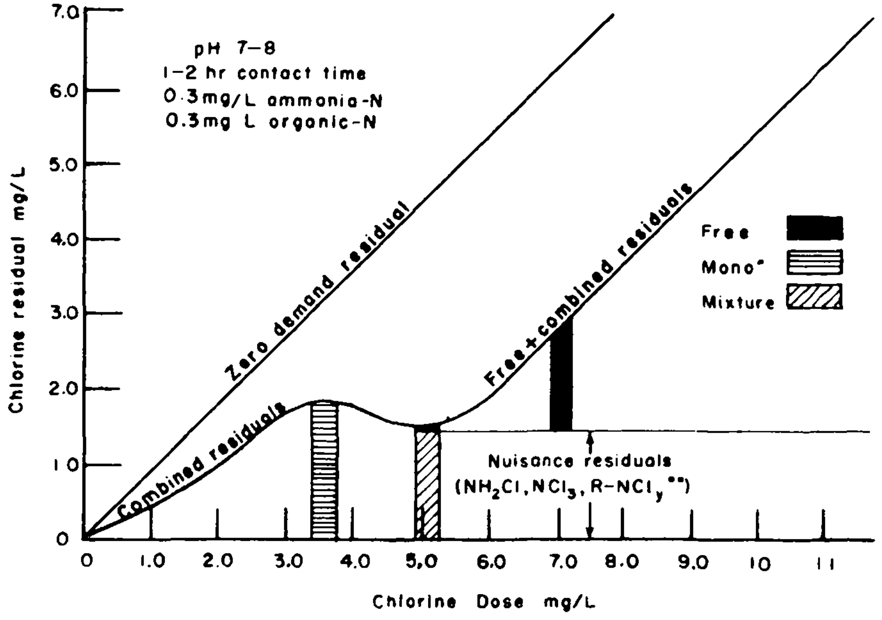
Taras[44] found that the total organic nitrogen consumed after chlorination follows a well-defined general pattern. The ammonia nitrogen is lost completely within one hour of contact time; the simple and unsubstituted amino nitrogen of many common amino acids is consumed more slowly over an extended period of time (many hours); protein nitrogen shows only a negligible loss, even after many days. Taras also demonstrated that this total nitrogen consumption is an exponential function of time

By way of contrast and clarification, it should be noted that the albuminoid nitrogen content of many simple amino compounds is reduced by as much as 75 percent within the first hour of contact with chlorine, but from proteinaceous matter the reduction is only very slight

Chlorination of this group of compounds is further complicated by the many varieties encountered. The particular protein involved will have a variable chlorine reaction, depending on the number of amino groups available for reaction with chlorine, which is a function of the peptide linkage in the protein. Therefore the chemistry of chlorination of organic nitrogen compounds is at best extremely complex because of the various hydrolysis products which may be encountered. Fortunately, most of the proteins are colloids that are partially removed in normal water treatment processes.

The significant difference between the reaction of chlorine with organic nitrogen compounds and that of ammonia is one of time, the comparative loss of nitrogen, and the formation of complex organic chloramines.

Both Griffin[13,14] and Williams[11] found that waters containing a mixture of both ammonia and organic nitrogen did not display the classic dip of the breakpoint reaction but, rather, a plateau effect. Fig. 4-9 illustrates what may be expected with a water containing 0.3 ppm ammonia nitrogen and 0.3 ppm organic nitrogen, with about 50 percent of the latter attributable to the simple amino acids and the rest proteinaceous matter. The results shown here are based largely on observa-



*Predominantly monochloramine; R-$NCl_y$ titrates as dichloramine
**R-$NCl_y$ = organochloramines

Fig 4-9 Relationship between ammonia nitrogen and organic nitrogen and chlorine tions by me and by Williams[11,27] and Palin.[24] Additional scientific evidence is needed to better predict the free available residual curve with waters characterized by significant amounts of organic nitrogen. Fig. 4-9 indicates very little drop in chlorine residual beyond the hump. This signifies two things: (1) continuing and competing reactions between mono- and dichloramine, and (2) very little loss of nitrogen—hence the plateau effect. Beyond the plateau, free available residual begins to appear; but note that the irreducible minimum residual is considerably greater than in the reaction with ammonia nitrogen (Fig. 4-5). Further, it is to be noted that the combined available residual can be made up of equal amounts of mono- and dichloramine, and as the ratio of chlorine to nitrogen increases, significant quantities of nitrogen trichloride can begin to form. This usually occurs when the Cl : $NH_3$–N ratio exceeds 14 : 1. Therefore these waters have the ability to produce: proportionately greater nuisance residuals; dichloramine, which contributes to taste problems; and nitrogen trichloride, which has an obnoxious odor. In some cases, the ratio of di- to monochloramine has been known to be 2 or 3 : 1 in the presence of excess free chlorine. The residuals in these systems are unstable, inasmuch as the free chlorine continues to react to decompose the mono- and dichloramine that are forming with the continued reaction with the organic nitrogen.

Another source of organic nitrogen which might play a significant part in the chlorination chemistry is the urea present in the raw water resulting from sewage discharge. Urea will hydrolyze, with the nitrogen breaking down to ammonia as one of the end products. This hydrolysis usually takes place in 3 to 4 hours under normal conditions; but if there is a lack of the urease enzyme, which breaks down urea, the formation of ammonia nitrogen is greatly inhibited. Urea does not form urea-chloramine at low concentrations, owing to its high dissociation constant,[45] but if a significant quantity of urea-N is present and hydrolysis proceeds at a slow rate, a situation of unstable residuals could easily result. The urea-N would be a reservoir for the production of ammonia to keep reacting with the free available chlorine. The role of urea in water chemistry is still rather obscure.

Another significant factor is the chlorine demand exerted by the carbon content of some of the simple amino acids, such as cysteine and glycine.[9] For glycine, Palin[24] noted that there were similarities to the chlorine-ammonia breakpoint phenomenon. Morris[9] work on the kinetics of chlorine and glycine reveal that up to a 1 : 1 molar ratio there is only a small loss of oxidizing chlorine. Beyond this ratio the loss of chlorine increases rapidly until it is complete at a molar ratio of 1.5 chlorine to 1 glycine. This is a lower ratio than the 2 : 1 for the chlorine-ammonia breakpoint system (10 : 1 by weight). At higher chlorine concentrations, there is a distinct departure from the chlorine-ammonia pattern. Significant amounts of oxidizing chlorine are not found in the solutions again until a molar ratio of 4 : 1 is reached. Upon analyzing the solutions, Morris[9] found it was the carbon, and not the nitrogen, that was being oxidized, when the molar ratios were 1.5 : 1 and 2 : 1. The original nitrogen was still present either as ammonia or as organic nitrogen. The oxidized carbon is released as carbon dioxide.

The reaction between chlorine and organic nitrogen, if given sufficient time, is certain to form organic chloramines of one kind or another. These chloramines display characteristics of dichloramine because they always appear in the dichloramine fraction when subjected to present amperometric and DPD-Ferrous titrimetric methods of analysis. Recent experience with completely nitrified and highly polished reclaimed wastewater reveals that a small fraction of these organic chloramines will intrude into the monochloramine reading.

Another reaction involving organic nitrogen and chlorine is the relationship between the organic chloramines and the monochloramine formed when ammonia-N is present. White et al.[70] found that there is a definite shift of the monochloramine fraction to the dichloramine (organic chloramine) fraction with time. This is probably caused by the disproportionation reaction of monochloramine, whereby HOCl is produced by the monochloramine, which then reacts with more organic N to form more organic chloramines. This causes a simultaneous reduction of monochloramines.

Some organic chloramines are known to hydrolyze to produce HOCl as one end product. The net result of organic chloramines is an overall reduction in the effectiveness of the total chlorine residual. In the free residual process they become a major portion of the nuisance residuals and are known to cause taste and odor problems.

## Chlorine Demand Research by Feben and Taras

**General Discussion.** To help recognize these systems as well as the general overall relationship between chlorine and nitrogenous compounds, Feben and Taras[46,47] in 1950 made a notable contribution in detailed study of the chlorine demand of Detroit water.

Taras pursued this work[44,48] during the next few years, and revealed a definite and significant relationship between chlorine demand and the character of the nitrogen compounds present. These findings are of such practical importance that they are presented here to demonstrate not only how the chemist can identify these troublesome compounds but also how the problem of organic nitrogen can be controlled.

Taras' findings are as follows:

1. There is a definite mathematical relationship between the amount of chlorine consumed in one contact period and that amount consumed in any other period.
2. A study of the constants in this mathematical relationship of chlorine consumed provides clues as to the nature of the nitrogen compounds reacting with the chlorine.
3. This mathematical relationship makes it possible to maintain specific chlorine residuals in the finished water.
4. The source of the chlorine-consuming nitrogenous compounds can be categorized as ammonia, amino acids, and proteins.

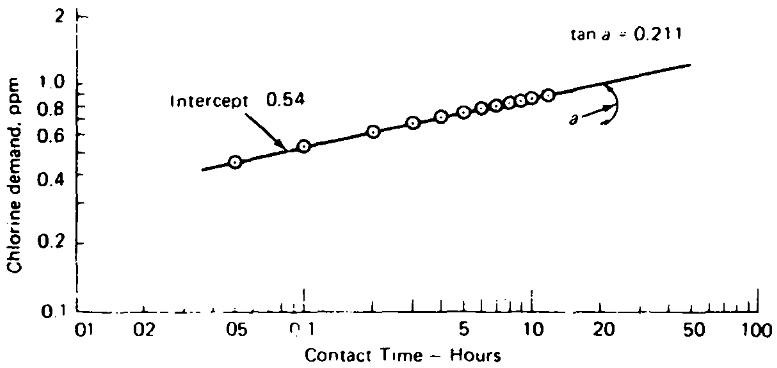


Fig. 4-10. Relationship between chlorine consumed and contact time.

5. The total nitrogen consumed follows a well-defined general pattern.

To find the mathematical relationship between chlorine consumed as a function of time (chlorine demand), a series of chlorine determinations are made on a sample of water with varying contact times from thirty minutes to thirty-six hours. These results are plotted on logarithmic paper, as seen in Fig. 4-10. In order to achieve such a plot, it is necessary for the chlorine dose to be sufficient always to provide a measurable residual at the end of the contact time.

**Mathematical Relationship.** It is preferable to use the amperometric method for determining chlorine residual. Two curves can be plotted: one for free chlorine residual; the other, for total chlorine residual. The results should plot in a straight line, which is of the general form:

$$D = kt^n \tag{4-54}$$

where

$D$ = chlorine demand ppm (chlorine dose − chlorine residual)
$t$ = chlorine contact time in hours
$k$ = chlorine demand after one hour ppm
$n$ = slope of curve (tan $a$)

For the example illustrated in Fig. 4-8, the equation then becomes:

$$D = 0.54t^{0.21} \tag{4-55}$$

This equation can be put into a more practical form if the 30-minute and 1-hour chlorine demands are known. Eq. (4-54) can be rewritten to read:

$$Dt = D_1 t^n \tag{4-56}$$

where $D_1$ is the chlorine demand after one hour contact, and $D$ is the chlorine demand after $t$ hours of contact. Then, when $t = 0.5$ hours, Eq. (4-56) can be written:

$$D_{0.5} = D_1 \times 0.5^n \tag{4-57}$$

and expressed logarithmically as:

$$\log D_{0.5} = \log D_1 + n \log 0.5 \tag{4-58}$$

then:

$$n = \frac{(\log D_1 - \log D_{0.5})}{-\log 0.5} \tag{4-59}$$

or:

$$n = \frac{(\log D_1 - \log D_{0.5})}{0.30103} \tag{4-60}$$

or:

$$n = 3.322\,(\log D_1 - \log D_{0.5}) \tag{4-61}$$

Substituting Eq. (4-61) in Eq. (4-56) it becomes:

$$D_t = D_1 t^{3.322(\log D_1 - \log D_{0.5})} \tag{4-62}$$

Eq. (4-62) may then be expressed in the logarithmic form:

$$\log D_t = \log D_1 + 3.322 \log t\,(\log D_1 - \log D_{0.5}) \tag{4-63}$$

or:

$$D_t = D_1 \left(\frac{D_1}{D_{0.5}}\right)^{3.322 \log t} \tag{4-64}$$

where

$D_t$ = chlorine consumed in $t$ hours (chlorine dose minus chlorine residual)
$D_1$ = chlorine consumed in one hour
$D_{0.5}$ = chlorine consumed in thirty minutes

With this equation, the chlorine demand at the end of any contact time $t$ can be determined, providing the chlorine demands at one hour and at thirty minutes are known.

**Practical Significance.** The usefulness of the basic equation derived from measuring chlorine residuals as plotted in Fig. 4-10 is the variation in the exponent value $n$. This reveals the speed of the reaction and gives a clue to the nature of the organic material involved in the reaction with chlorine. The inorganic ions ($NH_3^-$ $Fe^{++}$, $S^=$ etc.) all react almost instantaneously, causing rapid initial chlorine demand. This decreases the slope of the curve, so that the exponent $n$ approaches zero.

The higher the value of the exponent, the more complicated the organic material. For example, well waters generally show lower exponents (0.01 to 0.05) than do treated surface waters (0.10 to 0.20). This is because the nitrogen content of well water is mainly in the form of the inorganic ammonium ion, which reacts rapidly with chlorine, whereas surface waters generally suffer from sewage pollution and therefore contain the more complex compounds of amino acids and proteins.

In amino acids, the fifteen-minute chlorine demand is usually directly related to the amount of albuminoid nitrogen present. The exponential reaction constant as a function of time is dependent on the individual structure of the amino acid. An increase in the structural complexity results in higher values of the reaction constant $n$, Eq. (4-56), and will therefore exhibit prolonged chlorine demand.

Since the proteins are among the most complex compounds found in nature, they are difficult to decompose by chlorination. They have a high molecular weight and consist generally of 16 percent nitrogen, 50 percent carbon, 22 percent oxygen, and 7 percent hydrogen. Some contain as much as 2 percent sulfur; others, phosphorous and small amounts of iron. The presence of significant amounts of proteinaceous material in chlorinated water is indicated by a relatively high value of the reaction constant $n$. Some proteinaceous substances have yielded values of $n$ as high as 0.90.[47]

Therefore, by plotting on logarithmic paper the chlorine demand of various dosages versus contact time, the determination of the value of $n$ will serve as a clue to the nature of the nitrogen content present. A significant rise in the value of the exponent would indicate a rise in the organic nitrogen present and, further, a deterioration in the raw water quality.

The practical significance of organic nitrogen increase and its relation to chlorine demand, becomes a major parameter of raw water quality as follows:

1. Waters containing inorganic nitrogen (usually $NH_3$) are the easiest to handle. Stable chlorine residuals can be achieved after one hour or less contact time, depending on the nitrogen concentration.
2. Waters containing organic nitrogen will not produce stable residuals except after many hours of contact. This fact presents difficulties, because it means that the residuals leaving the confines of the plant are most likely unstable and that

special treatment procedures are required. The stability of these residuals depends upon the complexity of the proteinaceous compounds as well as upon their concentration. The amino acid group is identified by the albuminoid nitrogen, which is available for fairly rapid destruction by chlorination. This can usually be entirely destroyed by free residual chlorination in one to two hours; ammonia nitrogen, in thirty minutes to one hour. The proteins are identified by the total organic nitrogen, and are the most resistant to decomposition by chlorine. The residuals produced are the least stable of the three, inasmuch as oxidation reaction of chlorine continues for days.

These reactions are characterized by the loss of nitrogen when subjected to the appropriate analyses. For example, when the total nitrogen is in the form of the ammonium ion, the reaction with chlorine will produce a loss of almost 90 percent of the nitrogen. When the total nitrogen is in the form of both ammonia and albuminoid nitrogen, the loss may be only 75 percent or less, depending on the relative concentration of each. In sharp contrast to this is the almost negligible loss of nitrogen when it is present in the form of proteins.[44,49]

## CHLORINE AND OTHER INORGANICS

### Alkalinity

Since chlorine solutions are highly corrosive the application of chlorine to a process stream will often raise the question of chlorine corrosion. Corrosion by chlorine is related directly to *p*H, which is dependent upon alkalinity. Therefore it is appropriate to know the effect of chlorine on the alkalinity of a water.

If a water is dosed with chlorine to the extent of the chlorine demand of the water, all of the chlorine applied will end up as chloride ion ($Cl^-$) as follows:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \tag{4-65}$$

$$HOCl + Cl\ \text{demand} + HCl \longrightarrow 2HCl \tag{4-66}$$

This calculates as 1.4 parts alkalinity for each part chlorine:

$$2HCl + H_2O + CaCO_3 \longrightarrow CaCl_2 + CO_2 + 2H_2O \tag{4-67}$$

$$\text{Alkalinity} + CaCo_3 = \frac{100}{Cl_2} = \frac{100}{71} = 1.4$$

The reaction in Eq. (4-67) occurs at *p*H 4.3, which is the endpoint of the alkalinity titration, and where $CO_2$ exists.

When HOCl is not reduced, only one Cl goes to HCl and the reaction consumes just half of the alkalinity, or 0.7. As can be seen from the above, the subject of alkalinity destruction by chlorine is not a simple one.

Take the case of a water having sufficient alkalinity to maintain a 7.0 $pH$ and none of the chlorine applied is consumed by chlorine demand. In this case 50 percent of the chlorine applied will go to HCl. 80 percent of the remaining 50 percent will be undissociated HOCl and unreactive in the alkalinity reactions (see Table 4-4). However, the other 20 percent of the remaining 50 percent at $pH$ 7 is $H^+$ and $OCl^-$

The alkalinity reduction is calculated as follows:

$$50\% = (0.20 \times 50\%) = 60\% = 0.60$$

0.60 × 1.4 = 0.84 parts alkalinity reduction by chlorine at $pH$ 7.0.

The rule of thumb for alkalinity correction by the use of caustic to maintain $pH$ is a pound of caustic to a pound of chlorine.[82] One part of caustic produces 1.25 parts of alkalinity. If a water at $pH$ 7 is dosed with chlorine, and the demand is 6 mg/l, then the alkalinity reduction is 1.3 parts of alkalinity for each part of chlorine. This rule is reliable.

## Carbon

Chlorine reacts with inorganic carbon in much the same manner as it reacts with organic carbon. The reaction is rapid, and can be expressed:

$$C + 2Cl_2 + 2H_2O \longrightarrow 4HCl + CO_2 \tag{4-68}$$

This is the reaction that takes place in the dechlorination process using granular carbon filter beds. The production of HCl consumes approximately 2.1 parts of alkalinity as $CaCO_3$ for each part of chlorine removed. The weight ratio of chlorine to carbon is 1.0:0.0845.

## Cyanide

In an alkaline solution of $pH$ 8.5 or higher, chlorine reacts with cyanide to form cyanate. This is a primary step in treating plating wastes for the destruction of cyanides, and may be described as follows:

$$\begin{aligned} 2\,Cl_2 + \underset{\text{(caustic)}}{4\,NaOH} + \underset{\text{(cyanide)}}{2\,NaCN} &\longrightarrow \\ \underset{\text{(cyanate)}}{2\,NaCNO} + 4\,NaCl + 2\,H_2O& \end{aligned} \tag{4-69}$$

This reaction requires 2.73 parts of chlorine and 3.07 parts of caustic for each part of cyanide to convert to cyanate.

The complete destruction of cyanide by chlorine is usually carried out at a $pH$ of 8.5 to 9.5, and follows the following equation:

$$5\,Cl_2 + 10\,NaOH + \underset{\text{(cyanide)}}{2\,NaCN} \longrightarrow 2\,NaHCO_3 + 10\,NaCl + N_2 \uparrow + 4\,H_2O \tag{4-70}$$

The cyanide decomposes, liberating nitrogen as a gas; the carbon atom joins to form sodium bicarbonate. The other decomposition product is water. The weight ratio is 6.82 parts of chlorine and 7.69 parts of caustic to decompose one part of cyanide (CN).

## Hydrogen Sulfide

Hydrogen sulfide gas is frequently found dissolved in underground waters (rarely in surface supplies). It is also a constituent of septic sewage and is characterized by its obnoxious odor, best described as that of rotten eggs. It reacts instantaneously with chlorine either to precipitate free sulfur or to form dilute sulfuric acid. The determining factor in the formation of these end products is the *p*H.

Table 4-6 by Nordell,[50] shows how chlorine and hydrogen sulfide react at different *p*H levels.

The complete oxidation of hydrogen sulfide to the sulfate form is as follows:

$$H_2S + 4\,Cl_2 + 4\,H_2O \longrightarrow H_2SO_4 + 8\,HCl \tag{4-71}$$

Therefore 8.32 ppm of chlorine are required to oxidize 1 ppm of hydrogen sulfide to the sulfate form. However, the chlorine required to oxidize hydrogen sulfide to sulfur and water is only 2.08 ppm chlorine to 1 ppm hydrogen sulfide:

$$H_2S + Cl_2 \longrightarrow S \downarrow + H_2O \tag{4-72}$$

Table 4-6 Oxidation of Sulfides by Chlorine at Different pH Levels. (Contact time 10 minutes)

| *Final pH* | *Sulfides as ppm $H_2S$* | *$Cl_2$ Added mg/l* | *$Cl_2$ Residual mg/l* | *$Cl_2$ Consumed mg/l* |
|---|---|---|---|---|
| 3.2 | 5 | 50 | 6 | 44 |
| 5.0 | 5 | 50 | 7 | 43 |
| 6.2 | 5 | 50 | 7 | 43 |
| 6.4 | 5 | 50 | 9 | 41 |
| 6.8 | 5 | 50 | 11 | 39 |
| 7.1 | 5 | 50 | 18 | 32 |
| 7.6 | 5 | 50 | 18 | 32 |
| 9.0 | 5 | 50 | 25 | 25 |
| 10.1 | 5 | 50 | 25 | 25 |

(Amount of chlorine required to oxidize 5 ppm sulfides expressed as $H_2S$ is 8.32 × 5 = 41.6 mg/l.)

In this instance the sulfur precipitates as finely divided white particles which are sometimes colloidal in nature.

In Table 4-6 it can be seen that the sulfides were all oxidized to sulfates at $p$H values below 6.4. At $p$H around 7.0, about 70 percent was oxidized to sulfate and 30 percent to water and sulfur;* at $p$H values of 9 and 10, approximately 50 percent was oxidized to sulfate and 50 percent to sulfur and water.

It should be noted that for complete oxidation both sulfuric acid and hydrochloric acid are end products which will consume alkalinity. Each part of $H_2S$ oxidized in this reaction will consume 10 ppm alkalinity as $CaCO_3$. For the reaction which precipitates sulfur, only 2.6 mg/l alkalinity as $CaCO_3$ are consumed.

In actual practice, the destruction of hydrogen sulfide in potable water is not as simple as portrayed by the stoichiometric reactions of Eqs. (4-71) and (4-72)—there are side reactions which interfere with the production of the end products. (See Chapter 6.)

## Iron

The reaction of chlorine with iron is a very convenient one, since it can be used for two different purposes: to remove iron from water; to produce a coagulant for both water and sewage treatment.

In water supplies, iron is usually associated with underground waters and is generally in the form of ferrous bicarbonate, which is slightly soluble in water. Chlorine reacts with the ferrous ion and converts it to the ferric form. Depending upon the hydroxyl ion activity, the ferric chloride formed will quickly hydrolyze to ferric hydroxide. The latter precipitates as a reddish fluffy mass, depending on the concentration of ferric ion. Omitting the intermediate reaction of the formation of ferric chloride, the reaction is as follows:

$$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \longrightarrow 2Fe(OH)_3 + CaCl_2 + 6\,CO_2 \quad (4\text{-}73)$$

This reaction produces a rapid release of carbon dioxide, which causes a significant rise in pH. This reaction can proceed over a wide $p$H range (4 to 10), but the optimum is above 7. Each part of iron to be removed requires 0.64 parts of chlorine. This reaction consumes 0.9 parts of alkalinity as $CaCO_3$ for each part of ferrous ion oxidized to ferric ion. Either free or combined chlorine will produce this reaction, which is instantaneous for inorganic iron in solution. If the iron is in the form of an organic compound, the reaction is considerably inhibited.

It is often desirable to use the ferric ion as a coagulant in the water treatment process. This is most conveniently accomplished by converting the easy-to-handle ferrous ion to ferric by oxidation with chlorine. For example, pickle liquor, a

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* When chlorine is used to control $H_2S$ formation the treated water will likely appear milky due to the formation of free sulfur. This is known as the Tyndall effect.

by-product of steel mills, is the liquid form, and copperas the granular form, of ferrous sulfate commonly used with chlorine to make a coagulant, as follows:

$$6\ Fe\ SO_4 \cdot 7\ H_2O + 3\ Cl_2 \longrightarrow 2\ Fe\ Cl_3 + 2\ Fe_2(SO_4)_3 + 42\ H_2O \quad (4\text{-}74)$$

Each of the ferric salts will hydrolyze further to ferric hydroxide ($Fe(OH)_3$), utilizing the hydroxyl ion of the water and thus forming a brown gelatinous floc. To complete this reaction requires 7.8 parts of ferrous sulfate to each part of chlorine. The resulting solution will contain about 29.9 percent ferric chloride and 70.1 percent ferric sulfate. Each part of chlorinated ferrous sulfate consumes 0.54 parts of alkalinity as $CaCO_3$. This reaction proceeds over a wide pH range. With pickle liquor, adequate floc can be produced at as low as pH 4; however, the optimum should be kept at 7 or higher, since the resulting ferric hydroxide hydrolyzes more rapidly in this range.

## Manganese

Free available chlorine reacts to oxidize soluble manganese compounds, but chloramines or combined chlorine residuals have little effect. The oxidized manganese drops out as a precipitate in the form of manganese dioxide, as follows:

$$MnSO_4 + Cl_2 + 4\ NaOH \longrightarrow MnO_2 + 2\ NaCl + Na_2SO_4 + 2\ H_2O \quad (4\text{-}75)$$

This reaction requires 1.3 parts of free chlorine for each part of manganese oxidized, and 3.4 mg/l of alkalinity as $CaCO_3$ will be consumed. The reaction will proceed in a pH range of 7 to 10, with the optimum close to 10. It usually takes from two to four hours to reach completion. If the manganese is in the form of an organic complex, the reaction time will be even longer and unpredictable.

## Methane

Methane gas is sufficiently soluble in water to be both explosive and a fire hazard. Waters in this category are known to exist, and one of their characteristics is a high chlorine demand (10 to 25 mg/l). It was thought that chlorine reacted directly with methane to form carbon tetrachloride, as follows:

$$CH_4 + 4\ Cl_2 \longrightarrow CCl_4 + 4\ HCl \quad (4\text{-}76)$$

This reaction with elemental chlorine gas and methane gas is possible at temperatures of 300°C and higher. However, there is no reaction between methane and hypochlorous acid. The high chlorine demand of these waters is attributed to the presence of high amounts of oxidizable organics.

## Nitrites

**Chemistry of Formation.** The effect of nitrites on the chlorination process is often overlooked and misunderstood. Nitrites appear as transitory compounds when for a variety of reasons ammonia nitrogen is being oxidized to nitrates. The following equations illustrate the chemical pathways of this reaction.

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 4H^+ + H_2O \qquad (4\text{-}77)$$

Generally the *Nitrosomas* genera are involved in conversion of ammonium to nitrite under aerobic conditions. This is the reaction that often occurs within the biological slime on filter media.

The nitrites can be oxidized to nitrate generally by *Nitrobacter* according to the following reaction

$$2NO_2 + 2O_2 \xrightarrow{\text{bacteria}} NO_3 + 2N^+ + H_2O \qquad (4\text{-}78)$$

To oxidize 1 mg/l of ammonia nitrogen requires about 4.6 mg/l of oxygen (excluding synthesis of nitrifiers).

**Reaction with Chlorine.** Nitrites exert a significant chlorine demand in the presence of free chlorine as follows:

$$HOCl + NO_2^- \longrightarrow NO_3^- + HCl \qquad (4\text{-}79)$$

Since it takes two atoms of chlorine to make one molecule of HOCl it takes five parts of chlorine to oxidize one part of nitrite (as nitrogen). Therefore each mg/l of nitrite represents 5 mg/l chlorine demand in the presence of free chlorine. *However, a combined (chloramine) chlorine residual will not oxidize or react with nitrites.*

Nitrites are a deceptive factor in the chlorination process because they interfere with chlorine residual measurements. Apparently nitrites can oxidize KI to $I_2$. This is a reaction similar to that of free chlorine and chloramines. Therefore since there is no reaction between nitrites and chloramines, any residual measurement using the acid-iodide ($p$H $< 4$) procedure will show higher residuals when nitrites are present with chloramines.

When the phenylarsine oxide–iodine procedure is used (back titration) for measuring chloramine residuals the nitrites will be oxidized by the iodine solution used for back-titrating the PAO. Therefore the apparent chlorine residual will be higher than the true value (see Chapter 5).

## Seawater Chemistry

**Effect of Bromides.** The chemistry of seawater is unique when chlorination is involved owing to the presence of bromides in the seawater These bromide compounds result in a bromide ion content of 50–70 mg/l which will always be well in excess of any chlorine applied for chlorination purposes. A good example is the chlorination of seawater used for cooling water in an electric power generating station. Chlorination is used to control the marine growths in the steam condenser tubes because these growths interfere with the heat transfer efficiency of the condensers.

When the chlorine solution from a conventional chlorinator mixes with the seawater (*p*H 8.3) the chlorine reacts immediately with the bromide ions to form hypobromous acid[60,83]

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \qquad (4\text{-}80)$$

The rate constant ($K_o$) for this reaction is $2.95 \times 10^3$ liter per mol per sec. The hypobromous acid will dissociate, as does hypochlorous acid depending upon the *p*H, temperature, and ionic strength as follows:

$$K = \frac{(H^+)(OBr^-)}{(HOBr)} \qquad (4\text{-}81)$$

where

$$K = 2 \times 10^{-9} \text{ at } 20°C$$

The reaction rate between chlorine and the bromide ion, Eq. (4-80), is rapid. Using documented rate constants, Selleck[84] calculated the time required to convert 99 percent of the chlorine to bromine at a temperature of 25°C and a *p*H of 8.3* for various percentages of seawater. Fig. 4-11, taken from Selleck's calculations, shows that the reaction of Eq. (4-80) proceeds to 99 percent completion within 10 seconds in highly saline waters; i.e., 19,000 mg/l chlorides.

**Effect of *p*H.** The importance of *p*H in the reaction of chlorine species and the bromides in seawater must be emphasized. Free bromine ($Br_2$) is extracted from seawater and from the Dead Sea by chlorination:

$$Cl_2 + 2Br^- + 2H^+ \longrightarrow Br_2 + 2HCl \qquad (4\text{-}82)$$

However this reaction will not proceed to completion until the seawater is acidified to *p*H 4. (See Chapter 14.)

Chloramines will not oxidize bromides in either the neutral *p*H zone of 7–9 or in the acidic zone of 4–6. This is why the chlorine–ammonia process does not increase the TTHM potential when bromides are present in potable water.

At *p*H 4, chloramines will not oxidize the bromide ion to free bromine but

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* Seawater is always at *p*H 8.3 in the salinity range of 12,000–19,000 mg/l chlorides.

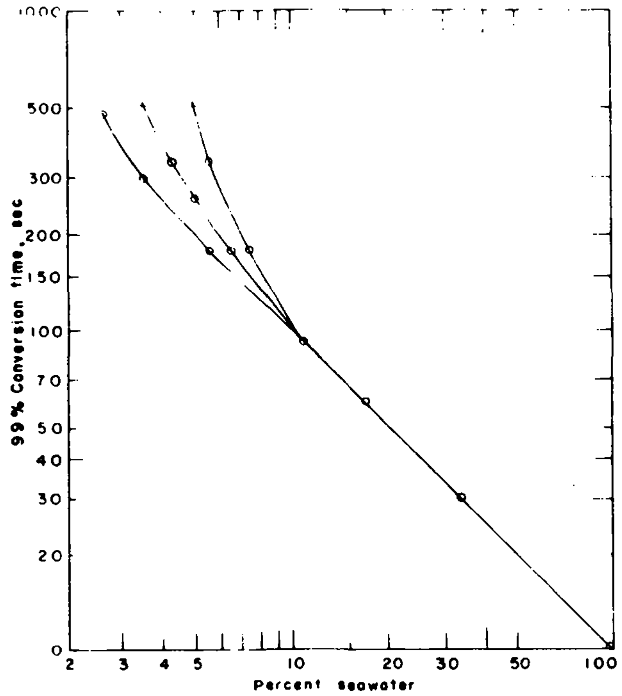

Fig. 4-11 Time required for 99 percent conversion of free chlorine to HOBr at 25°C and pH 8.3[86] (courtesy *Journal WPCF*)

HOCl will. This bit of fundamental chemistry is the basis for the invention of a free chlorine residual analyzer that is not affected by the presence of chloramines. (See Chapter 9.)

**Dissociation of Hypobromous Acid.** This is a salient factor in the chlorination of seawater because HOBr is an effective biocide. This must be assumed because all seawater chlorination studies have reported residuals as chlorine, when in reality the residuals are most likely to be a mixture of bromine species. Seawater chlorination has been practiced by the electric power industry for six decades, and the success of this practice of reporting residuals as chlorine for the control of marine growths is sufficient evidence to conclude that the resulting bromine species are potent biocides. The dissociation of HOBr plays an important role. Some comparative experiments have been made on coliform destruction using chlorine generated from seawater versus chlorine solution with freshwater and conventional chlorination equipment These experiments tended to show a better coliform kill with on-site generated hypochlorite from seawater

The explanation might be found in the dissociation of HOCl vs. HOBr From

Eq. (4-81) it can be calculated that at $pH$ 8, the undissociated HOBr is 83 percent vs. HOCl at only 28 percent

**Effect of Ionic Strength.** Since seawater chlorination produces species of bromine residuals owing to excess bromide ions present in seawater, the dissociation values for HOCl based upon ionic strength of seawater cannot be used. From the dissociation value for HOBr described above the ionic strength of seawater ($I = 1.0$) will have little effect on the potency of the undissociated HOBr.

**The Role of Ammonia Nitrogen.** The presence of ammonia nitrogen in seawater complicates the chemical reactions between the chlorine species and the bromides. When this situation occurs there will be two competing reactions operating simultaneously These reactions are: (1) chlorine reacts with the ammonia N practically instantaneously at $pH$ 8.3 to form chloramines, and (2) the chlorine will react at about the same speed with the bromide ion. However, since the bromide ion concentration is on the order of 50–70 mg/l and the ammonia-N not more than 2–3 mg/l, the chlorine–bromide reaction might be the faster. The result is probably the immediate formation of both monochloramine and hypobromous acid. These two compounds start another round of reactions as follows:

$$NH_2Cl + Br^- + 2H_2O \longrightarrow HOBr + NH_4OH + Cl^- \tag{4-84}$$

$$HOBr + NH_4OH \longrightarrow NH_2Br + 2H_2O \tag{4-85}$$

$$NH_2BR + HOBr \longrightarrow NHBr_2 + H_2O \tag{4-86}$$

$$NHBr_2 + H_2O \longrightarrow NOH + 2H^+ + 2Br^- \tag{4-87}$$

The intermediary NOH formed in Eq. (4-87) is the catalyst which allows the dibromamine to trigger the breakpoint as follows:

$$NHBr_2 + NOH \longrightarrow N_2 + HOBr + H^+ + Br^- \tag{4-88}$$

The reactions described by Eqs. (4-84) through (4-88) are sequential and rapid. Very little monobromamine is formed. Moreover there is no evidence of tribromamine formation. The most significant aspect of the above reaction is the rapid formation of dibromamine, which triggers the breakpoint. Selleck points out that due to the presence of excess bromide ion the removal of ammonia nitrogen from seawater by these reactions is independent of the molar ratio of HOBr to $NH_3$ –N.[85] Therefore the presence of ammonia-N in seawater does not present any problems for the chlorination process.

The above reactions take place only in the range of seawater $pH$, 8.3.

## GERMICIDAL SIGNIFICANCE OF CHLORINE RESIDUALS

### Introduction

Studies have been made on the nature of the killing mechanism of chlorine on bacteria,[20,51-54] cysts,[20,55,56] and spores.[20,57] The inactivation mechanism of viruses by chlorine and other oxidants has never been resolved. An infective virus particle or virion consists of a core composed of or containing one kind of nucleic acid which is encased in a protein shell or capsid. The capsid is built from a number of morphological subunits identified as capsomeres. It is thought that the oxidant penetrates the capsid by chemical transformation and then attacks the nucleic acid.

Exactly how chlorine kills bacteria, cysts, and spores is still an academic puzzle. During the period of its early use (circa 1910) as a disinfectant, it was believed that the germicidal power of chlorine was due solely to the liberation of nascent oxygen from the hypochlorous acid formed by the reaction of chlorine and water ($HOCl \rightarrow HCl + O$). This theory led to considerable confusion on the subject and thwarted many serious investigations. It was not until 1944 that Chang[56] dispelled this belief by showing that hydrogen peroxide and potassium permanganate liberated considerable quantities of nascent oxygen but showed little germicidal efficiency. He further proved that there was no liberation of oxygen involved in the chlorine reaction, and that the disinfecting agent is hypochlorous acid. He favored the formation of the toxic substance theory.

In 1946, Green and Stumpf[51] concluded that chlorine reacted irreversibly with the enzymatic system of bacteria, thereby killing the bacteria. They were able to show that a bacterial suspension became sterile when bacteria lost the power to oxidize glucose. They also found that when the enzymes which contain sulfhydril groups were oxidized by chlorine, the oxidation was irreversible, thus abolishing enzyme action and resulting in the destruction of the bacteria, and that the most significant of this group is the enzyme triosephosphate dehydrogenase. In 1953, Ingols et al.[58] concurred with this theory, but, using monochloramine, they found that even though they restored the sulfhydril groups the bacteria were not restored. This led them to believe that while the sulfhydril group may be the most vulnerable to a strong oxidant like hypochlorous acid or chlorine dioxide, there were changes in other groups caused by monochloramine and dichloramine which may be important in bringing about death to bacteria.

More recently (1962), Wyss[54] has pointed out that probably the effective mechanism of death to microorganisms is the phenomenon of unbalanced growth. That is, destruction of part of the enzyme system will so throw the cell out of balance that by progress of its own metabolism the cell dies before the necessary repairs are made

Whatever the chemical action, it is generally agreed that the relative efficiency of various disinfecting compounds is a function of the rate of diffusion of the active agent through the cell wall. Fig. 4-12 shows the essential elements of a bacterial cell. It is assumed that after penetration of the cell wall is accomplished, the disinfecting compound has the ability to attack the enzyme group whose destruction results in death to the organism. Factors which affect the efficiency of destruction are:

1. Nature of disinfectant (kind of chlorine residual fraction)
2. Concentration of disinfectant
3. Length of contact time with disinfectant
4. Temperature
5. Type and concentration of organisms
6. *p*H

## Hypochlorous Acid

HOCl is the most effective of all the chlorine residual fractions. This fraction is known officially in the industry as free available chlorine residual.[59,60] Hypochlorous acid is similar in structure to water; hence, the formula HOCl is preferred to HClO. The germicidal efficiency of HOCl is due to the relative ease with which it can penetrate cell walls. This penetration is comparable to that of water, and can be attributed to both its modest size (low molecular weight) and to its electrical neutrality (absence of an electrical charge).

Other things being equal, the germicidal efficiency of a free available chlorine residual is a function of the pH, which establishes the amount of dissociation of HOCl to $H^+$ and $OCl^-$ ions. Table 4-4 shows the percentage of undissociated HOCl in a chlorine solution for various *p*H values and temperatures. Lowering

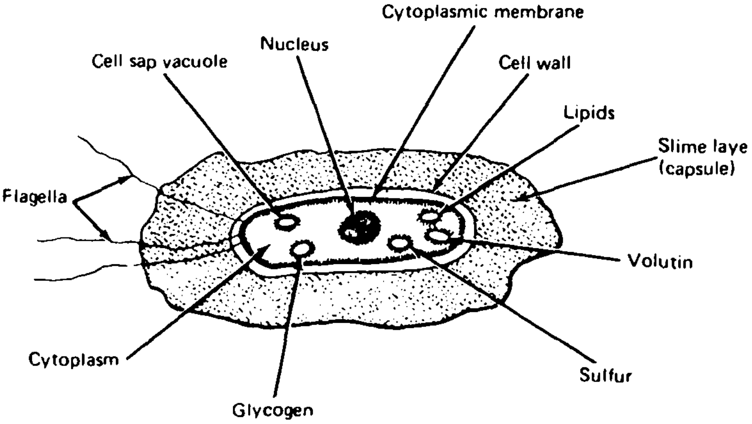

Fig. 4-12 Schematic diagram of a bacterium.

the temperature of the reacting solution suppresses the dissociation; conversely, raising the temperature increases the amount of dissociation.

The rate of dissociation of HOCl is so rapid that equilibrium between HOCl and the $OCl^-$ ion is maintained, even though the HOCl is being continuously used. For example, if water containing 1 mg/liter of titrable free available chlorine residual has been dosed with a reducing agent that consumes 50 percent of the hypochlorous acid, the remaining residual will redistribute itself between HOCl and $OCl^-$ ion according to the values shown in Table 4-4. This is commonly referred to as the "reservoir" effect.

## Hypochlorite Ion

The $OCl^-$ ion, which is a result of the dissociation phenomenon, is a relatively poor disinfectant, because of its inability to diffuse through the cell wall of microorganisms. The obstacle to this passage is the negative electrical charge, as substantiated to some extent by the fact that the activation energy for disinfection by HOCl is in the range of those for diffusion ($E$ = 7,000 calories), whereas that of the $OCl^-$ ion is more characteristic of a chemical reaction ($E$ = 15,000 calories). The relative efficiencies of HOCl and the $OCl^-$ ion have been well documented by Professor Fair and his colleagues at Harvard.[20,37] These findings took into consideration the work done by Butterfield et al.[61] in 1943 and by Butterfield and Wattie[62] in 1944. This was a concerted effort to relate disinfection to chemistry.

It is well known that the disinfecting efficiency of free available chlorine residual decreases significantly as the $p$H rises. At a $p$H above 9 there is little disinfecting power. At this $p$H level and at 20°C, 96 percent of the titrable free available chlorine will consist of the $OCl^-$ ion. This is an indication of the low germicidal efficiency of the $OCl^-$ ion. The Harvard group developed an equation devised to calculate the total free available chlorine residual required to kill a given percentage of a specified organism. This equation requires the use of a constant, which is the ratio of germicidal efficiency of the $OCl^-$ ion to HOCl:

$$R = A\frac{1 + [K_i/(H^+)}{1 + B[K_i/(H^+)]} \qquad (4\text{-}89)$$

where

$R$ = the required total titrable available chlorine residual.
$A$ = the amount of HOCl alone (expressed as titrable chlorine) required to destroy the bacteria
$K_i$ = the dissociation constant of HOCl for a given temperature
$B$ = the ratio of the efficiency of $OCl^-$ to HOCl.

Fair et al.[59] observed concentrations of titrable free available chlorine required to kill 99 percent *Escherichia coli* in 30 minutes at 2–5°C at different $p$H values:

$$R = .005\frac{1 + [2.2 \times 10^{-8}/(H^+)]}{1 + 0.012[2.2 \times 10^{-8}/(H^+)]} \tag{4-90}$$

The value of $B$ used (0.012) indicates that the $OCl^-$ ion is about 1/80 as efficient as HOCl for the conditions stated. This is not in very close agreement with investigations by Selleck, University of California, Berkeley. His work demonstrates that the $OCl^-$ ion is only 20 times less effective than HOCl rather than 80 times.[63]

A similar investigation was made on the destruction of cysts, and further demonstrated the greater efficiency of HOCl over the $OCl^-$ ion. Experimental cysticidal residuals were obtained for a 100 percent destruction of thirty cysts per ml of *Endamoeba histolytica* over a temperature range of 3–23°C and with a contact time of 30 minutes. The relative efficiencies of the $OCl^-$ ion to HOCl for inactivation of cysts are summarized as follows·

| Temperature, °C | $OCl^-$ to HOCl Relative Effective Ratio |
|---|---|
| 3 | 1/150 |
| 10 | 1/200 |
| 18 | 1/250 |
| 23 | 1/300 |

Similarly, Eq. (4-89) can be used to calculate the amount of $R$ required to destroy this organism under specific conditions of temperature contact time and $p$H. Since cysts are the most difficult miroorganisms to destroy with a chlorine residual, it is reasonable to expect that other organisms, such as spores and viruses, would show a relative effective ratio of the $OCl^-$ ion to HOCl somewhere between the extremes of *Esch. coli* at 1/20 and *E. histolytica* at 1/300. It is evident that because of this effective ratio the low germicidal efficiency of $OCl^-$ must be taken into account and that the effectiveness of free available chlorine residual is seriously impaired when the $p$H exceeds 9.0. The reason for this is obvious. At $p$H 9 and a temperature of 15°C the percentage of HOCl in a given solution is 4.13; at $p$H 7.5 it is 57.68. (See Table 4-4.) This prevails in spite of the HOCl "reservoir" effect.

## Chloramines

**Background Discussion.** That chloramines are slower to kill microorganisms than free available chlorine has been common knowledge for some time. Probably the first person to become aware of this was Alexander Houston[64] in 1925. The first scientific laboratory work on the germicidal efficiency of chloramine was done by K. Holwerda[28] at the Laboratory for the Purification of Water at Manggarai in the Dutch East Indies. His work investigated chloramines at $p$H 4.5, 6.8, and 8.5. At $p$H 4.5, the chlorine compound would most likely be 100 percent dichloramine (see Fig. 4-4); at $p$H 8.5, it would probably be 100 percent monochloramine

Holwerda's findings indicated a time factor as high as 80 : 1 required for monochloramines over free available chlorine, and as low as 20 : 1 for the same germicidal efficiency This compares with Butterfield and Watties' findings[62,65,66] that chloramine required approximately a hundredfold increase in contact time over free available chlorine at $pH$ 9.5 Kabler[67] also concluded that, to obtain the same kill with same amounts of free available and combined available chlorine residual, the latter required 100 times more exposure time.

The above historical data have categorized chloramines as a poor disinfectant compared to free chlorine However, recent studies indicate that if chloramines are allowed contact times of 45–60 minutes they are able to match the efficiency of free chlorine based upon the destruction of coliform organisms. (See Chapter 8.)

**Monochloramine.** From the work by Butterfield and Wattie mentioned above, and later confirmed by Kabler, it might be concluded that for the same conditions of contact time, temperature, and a $pH$ range of about 6–8, it will take at least 25 times more combined available chlorine than free available chlorine to produce the same germicidal efficiency. Furthermore, it can be assumed that if the chlorine to ammonia nitrogen ratio is less than 5 : 1 and if the $pH$ is 7.5 and higher, the combined residual will probably be 100 percent monochloramine. This difference in potency of monochloramine and HOCl might be explained by the difference in their oxidation potentials, assuming that the action of chloramine is of an electrochemical nature rather than one of diffusion, as seems to be the case with HOCl. (See Fig. 4-16.) The work of Ingols et al.[58] might also explain the difference between free available and combined available chlorine residuals. They indicated that by using monochloramine only, its reaction with vulnerable enzyme groups (in bacteria) may be a reversible reaction. Another explanation of the low potency of monochloramine is that it may be a function of hydrolysis. The hydrolysis constants of chloramine in general can be expressed as follows:

$$K_n = \frac{(\mathrm{HOCl})(\mathrm{RR'NH})}{(\mathrm{RR'NCl})} \qquad (4\text{-}91)$$

From this equation it can be seen that one of the products of hydrolysis is free available chlorine (HOCl), which tends to be low in strong solutions, but which increases in weak solutions.[16] The hydrolysis constant of monochloramine, as determined by Corbett, Metcalf, and Soper, was found to be $K_n = 2.8 \times 10^{-10}$ at 15°C in accordance with:

$$\mathrm{NH_2Cl + H_2O \rightleftharpoons NH_3 + HOCl} \qquad (4\text{-}92)$$

This is in fair agreement with more recent work by Morris[69] who found that $K_n = 1.0 \times 10^{-11}$ (approximately). These two investigations were carried out under quite different conditions: Corbett et al. performed their study at $pH$ 14 and $10^{-2}M$; Morris, at $pH$ 5 and $10^{-4}M$. Morris calculates that a pure solution of $NH_2Cl$ at a concentration of 2.0 mg/l as chlorine ($2.82 \times 10^{-5}M$) will be 0.58 percent hydrolyzed at $pH$ 7 and 25°C.

However, the work done at the San Jose/Santa Clara Water Pollution Control Plant[70] over a two-year period (1980–1982) indicates that monochloramine has a much greater germicidal efficiency than described above. This investigation demonstrated clearly that in a completely nitrified effluent monochloramine residuals based upon a chlorine to ammonia-N ratio of 6:1 can achieve coliform kills equivalent to free chlorine residuals of the same concentration and the same contact time, i.e., 50 minutes.*

Other experiences quoted elsewhere indicates that monochloramine can be equivalent to free chlorine provided the contact time is at least 45–60 min. and the Cl:N ratio is 6:1. The potency of monochloramine may be a function of its slow rate of diffusion through the bacteria cell wall, the hydrolysis product HOCl, or its redox potential.

It is generally concluded that ammonia chloramines formed when $NH_3$-N is present in the water (or wastewater) will slowly hydrolyze with time to produce HOCl, which then reacts with organic N present to form organic chloramines. Since the organic chloramines are considered to be relatively ineffective germicides this would explain the phenomenon of decreasing (with time) germicidal efficiency of a combined chlorine residual in a wastewater effluent.

**Dichloramine.** Although Holwerda was probably not aware of it, his work definitely demonstrated that dichloramine is a more potent germicide than monochloramine. At $pH$ 4.5 and with 0.5 mg/l chloramine (probably 100 percent dichloramine) disinfection was achieved in twenty minutes, whereas at pH 8.6 (probably 100 percent monochloramine) it required sixty minutes. This was based upon the observance of gas formers. On another series using plate counts, it was ten minutes at pH 4.5 and sixty minutes at pH 8.6 to achieve a one plate count with the control showing 388.

Fair et al.[20] found that at $pH$ 4.5, which they observed to be 100 percent dichloramine (see Fig. 4-4), a residual of 2.0 mg/l gives a 100 percent kill of cysts (*E. histolytica*); whereas at pH 10.0, when only monochloramine is present, the required cysticidal residual is approximately 7.5 mg/l. They used a concentration of 30 cysts/ml at a temperature of 23°C and a contact time of thirty minutes. Their overall results with cysts show that dichloramine is about 60 percent and monochloramine about 22 percent as efficient as HOCl. Because of the formation of the relatively ineffective $OCl^-$ ion in HOCl solutions at high pH values, the chloramines are more efficient cysticidal agents above a pH of about 9. On the limited number of experiments performed with spores of *B. anthracis*, dichloramine showed an

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* $NH_4OH$ added to nitrified affluent

efficiency of 15 percent that of HOCl for a thirty-minute contact period, while the efficiency of monochloramine was too low to be measured.[20]

Kelly and Sanderson[34] attributed the inactivation of poliomyelitis and coxsackie viruses to dichloramine rather than to monochloramine. They were able to achieve 99.7 percent inactivation with a combined available chlorine residual in three hours at *p*H 6, while at *p*H 10 it required six to eight hours for polio virus. They determined that dichloramine was 43 percent of the total at *p*H 6 and, at *p*H 10, was 32 percent. (See Fig. 4-4.) Although these fractions were determined by the amperometric method, the results vary widely from the curve by Fair et al., which was determined by a more sophisticated method—light absorbence as measured by a spectrophotometer.

It can probably be concluded from all these data that dichloramine is twice as potent as monochloramine as a germicidal agent. However, additional scientific data are necessary to establish this as a fact. This would be a welcome contribution to the field of wastewater chlorination. However, in water treatment it is of only academic interest, since dichloramine is to be avoided because it contributes to taste and odor problems. Moreover it is doubtful that there ever would be a condition whereby a pure dichloramine residual could be isolated and measured as such. Those residuals that exhibit themselves as dichloramine via all of the well known analytical procedures are probably a mixture of organochloramines and not a specific specimen of dichloramine. This is the weakness and failure of the analytical procedures. A pure dichloramine made in the laboratory is unstable in the presence of HOCl. It is quite conceivable that in waters lacking organic nitrogen but containing ammonia-N, pure dichloramine will form in the free residual process. However, it will disappear when the competing reactions pass beyond the breakpoint zone.

To date there are no analytical methods that can identify pure dichloramine as differentiated from the organochloramines that appear in the dichloramine procedure.

**Nitrogen Trichloride.** This chlorine compound is known to be an effective oxidizing agent. It has been used for over thirty years in the bleaching of flour, as a fungicide, and for control of insect pests on fruit in storage rooms and cars during shipment. Its oxidation potential and its bactericidal efficiency has never been evaluated, but this compound may possibly contribute substantially to the oxidation of organic matter and destruction of microorganisms in water and wastewater chlorination in those instances when it does appear. Nitrogen trichloride mparts an objectionable taste and a foul odor when present in potable water. Fortunately it is unstable in sunlight and highly insoluble in water, and aerates asily. It is characterized by its pungent chlorine-like odor. It causes severe eye earing in low concentrations. It is difficult to capture by any analytical procedure—t is too volatile. Nitrogen trichloride cannot exist without the presence of HOCl. t has been known to form in the distribution system long after leaving the treatment lant. This situation can be corrected by converting the free chlorine residual to chloramines by post-ammoniation However, the preferred method is complete dechlorination of the finished water followed by rechlorination.

It is never necessary to determine the concentration of $NCl_3$ present. The operator needs only to know if it is there. This is easily determined by human responses, either by the eyes tearing or by its odor. It is the only chlorine species that causes tearing of the eyes.

## Organic Chloramines

**General Discussion.** This discussion *excludes* the manufactured organic chloramines used for sanitizing purposes and swimming pool treatment; i.e., the chloroisocyanurics, chlorinated hydantoins, etc. These compounds have hydrolysis constants as high as $10^{-4}$ They will yield HOCl concentrations equivalent to hypochlorites of the same available chlorine content.[16] This is achieved by hydrolysis at a slow but steady rate.

The organic chloramines of interest here are those that are formed during the chlorination of potable water or wastewater. These organochloramines are directly related to the organic nitrogen content in potable waters, which varies from a trace up to a maximum of 3 mg/l. Any concentration greater than 0.25 is certain to cause taste and odor problems.

Well oxidized secondary effluents will contain from 10 to 15 mg/l organic N. Well polished filtered and nitrified effluents will contain from 1 to 3 mg/l organic N.

These chloramines can be measured by forward titration using either the amperometric or DPD-Ferrous titrimetric method. They will appear in the dichloramine fraction. These chloramines have relatively little or no germicidal efficiency, hence the term: nuisance residuals.

**Recent Studies of Germicidal Efficiency.** As early as 1966 Feng[87] discovered a great disparity in the germicidal efficiency between ammonia chloramines and those found in an environment of pure organic nitrogen compounds. He has reported that methionine, which is one of the indispensable amino acids for biological growth, and is expected to be present in wastewater, forms a measurable chlorine residual with no germicidal power. Feng also investigated the lethal activities of the glycine, taurine, and gelatin chloramines. His work shows that taurine chloramines are as lethally active as ammonium chloramines at *p*H 9.5, but that their germicidal efficiency falls off as the *p*H decreases. The glycine chloramines are as germicidally active as monochloramine at *p*H 4 but are totally inert at *p*H 7, and the gelatin chloramines are active at *p*H 9.5 but are inert at *p*H 7 and 4. There are certain to be other such organic nitrogenous compounds which contribute to the total chlorine residual which have little or no germicidal effect.

Sung[88] made a controlled laboratory study of fifteen organic compounds representing seven groups to evaluate their individual and combined effect upon the chlorination process. Nine of the fifteen compounds were found to interfere with the germicidal efficiency of the chlorination process. Of these nine compounds five were organic nitrogen compounds. Cystine and uric acid were the severest inhibitors of the nitrogen group. When five of the interfering compounds were mixed together, their combined effect was found to be more pronounced than any of their individual effects, but did not equal the sum of their individual effects. Sung compared the germicidal efficiency of a simulated wastewater with and without the interfering organic compounds. He found that the germicidal efficiency of wastewater containing the interfering compounds by themselves and the resulting chlorine residuals had little or no germicidal effect. The greatest interference was observed to be caused by cystine, tannic acid, humic acids, uric acids and arginine.

*Cystine* is an amino acid connected by two sulfur groups that is known to react with chlorine. Tannic, humic and uric acids are capable of exerting a significant chlorine demand when present in water or wastewater. *Arginine* is a basic amino acid. The reaction between chlorine and arginine is almost instantaneous.

The organic compounds that had little or no interfering effects on the chlorination process were: acetic acid, cellubiose, dextrose, glutamic acid, uracil, and lauric acid.

The significance of the above findings by Sung[88] confirms the theory of interference in the chlorination process by the presence of organic nitrogen. It further points to the fact that present analytical techniques do not provide for separating the chlorine residual fractions into those of equal germicidal efficiency.

It is also interesting to note that Esvelt, Kaufman and Selleck[89] found that the toxicity of combined chlorine residuals diminished with time. This finding together with those of Sung[88] demonstrates quite convincingly that there are a significant number of organic compounds in wastewater which will react with chlorine to form organic chloramines of little or no germicidal potential, and moreover, these compounds appear to increase in concentration with time. This apparent increase of this chlorine residual fraction with time would also explain the loss of germicidal efficiency of combined chlorine residuals in wastewater with time. The supposition is that the predominantly monochloramine residual present hydrolyzes to form free chlorine (HOCl), and both the monochloramine and HOCl react with the organic nitrogen compounds to form the ineffective organic chloramines.

**Nuisance Residuals.** These are the residuals, other than free chlorine (HOCl), which appear beyond the breakpoint. This is Zone 3 in Fig. 4-4. They usually consist of chloramines that titrate in the dichloramine fraction. As described before they are probably made up of mostly organic chloramines.

At the breakpoint there are at least three competing reactions which tend to produce free chlorine, monochloramine, dichloramine, and nitrogen trichloride. Pure dichloramine is unstable in the presence of free chlorine; nitrogen trichloride cannot form without free chlorine; and monochloramine is almost always present of the germicidal efficiency of the different fractions of available chlorine residual when nitrogen trichloride is formed. Therefore a reasonably good guess as to the composition of nuisance residuals in actual practice might be: (1) When $NCl_3$ is formed, 85–90 percent organic chloramines, 8–12 percent monochloramine, and 2–3 percent $NCl_3$; (2) when $NCl_3$ is absent, 90 percent organic chloramines and 10 percent monochloramine.*

## Investigators Consensus of Germicidal Efficiency

In 1964 Clarke, Berg, Kabler, and Chang[71] prepared graphics (see Fig. 4-13) showing the relative germicidal efficiency of HOCl, $OCl^-$, and monochloramine. These curves represent a composite of available data adjusted to yield a common base for comparison, and are presented here to summarize the preceding discussion

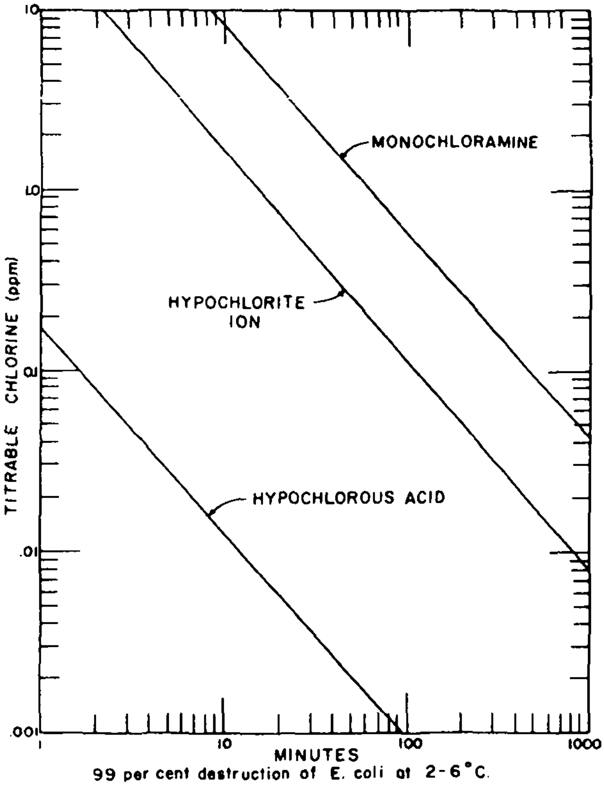

Fig. 4-13 Comparison of germicidal efficiency of hypochlorous acid, hypochlorite ion, and monochloramine.

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* Organic chloramines that appear in the dichloramine fraction of the forward amperometric titration procedure are known to intrude into the monochloramine fraction. This distorts the monochloramine reading

of the germicidal efficiency of the different fractions of available chlorine residual Scientific data are lacking to properly locate on this curve the germicidal efficiency of the dichloramine and nitrogen trichloride fractions.

It should be noted that these curves represent chlorine dosages applied to chlorine demand-free solutions sufficient to achieve only a 2 log reduction at very low temperatures and unreported contact times. The lower end of the curves may not be completely reliable. Full scale plant operation on water reuse situations have demonstrated that for contact times of 45–60 minutes and 4–5 log reductions of coliforms, monochloramine residuals are almost equal to free chlorine residuals and in some cases superior to free chlorine. This anomaly is described in Chapter 8.

## Morris' Lethality Coefficient

In 1967 Morris[72] presented a tabulation of germicidal concentrations giving 99 percent (2 logs) inactivation within ten minutes contact time. From this Morris derived a lethality coefficient:

$$\lambda = 0.46/C_{99:10}$$

where $C$ is the concentration of the chlorine compound in mg/liter The values of λ computed from this 1967 tabulation are shown in Table 4-7.

This tabulation illustrates the superiority of free chlorine over both monochloramine and the hypochlorite ion. This is an interesting and useful comparison, but here again the organism destruction is based upon a short contact time (10 min) and only 2 logs removal. From plant operation experience White believes that longer contact times and greater total coliform removals (4–5 logs) closes the gap between the germicidal efficiency of free chlorine and monochloramine. This has been demonstrated by Prof. R. E. Selleck, University of California,[73] Sanitation Districts of Los Angeles County,[74] and the San Jose/Santa Clara, CA Water Pollution Control Plant.[70] (See Chapter 8.)

# ELECTROCHEMICAL PROPERTIES OF CHLORINE RESIDUALS

## Introduction

General dissatisfaction with the orthotolidine method of measuring chlorine residuals led a number of investigators to try the oxidation–reduction potential concept for evaluating the germicidal efficiency of the various species of chlorine residuals. This concept is commonly referred to as ORP or redox systems. In its simplest terms it is an electrode potential reading.

The originators of this method as it related to the chlorination of water were Rideal and Evans,[75] who suggested it as early as 1913 They believed that the germicidally active chlorine could best be measured by the potential created across

Table 4-7 Values of λ at 5°C*

| *Species* | *Enteric Bacteria* | *Amoebic Cysts* | *Viruses* | *Spores* |
|---|---|---|---|---|
| HOCl as $Cl_2$ | 20 | 0.05 | 1.0 up | 0.05 |
| $OCl^-$ as $Cl_2$ | 0.2 | 0.0005 | <0.02 | <0.0005 |
| $NH_2Cl$ as $Cl_2$ | 0.1 | 0.02 | 0.005 | 0.001 |

* λ in $(mg/liter)^{-1}$ $(min)^{-1}$

an electrode system in the solution. Most investigators studying the disinfecting power of chlorine found that its efficiency varies widely under different conditions. The chief factor influencing the efficiency of free chlorine (HOCl) is the *p*H of the solution.

In 1933 Schmelkes[76] demonstrated that the level of potential of a chlorine residual does in fact affect its germicidal efficiency and that the potential is related to *p*H, chlorine concentration, and the ratio of chlorine to ammonia.

Fig. 4-14 shows that free available chlorine has a much higher potential than do chloramines and it varies with *p*H.

Fig. 4-15 shows the relationship between the chlorine–ammonia ratio and potential level, indicating again the lower potential of the chloramines. During these

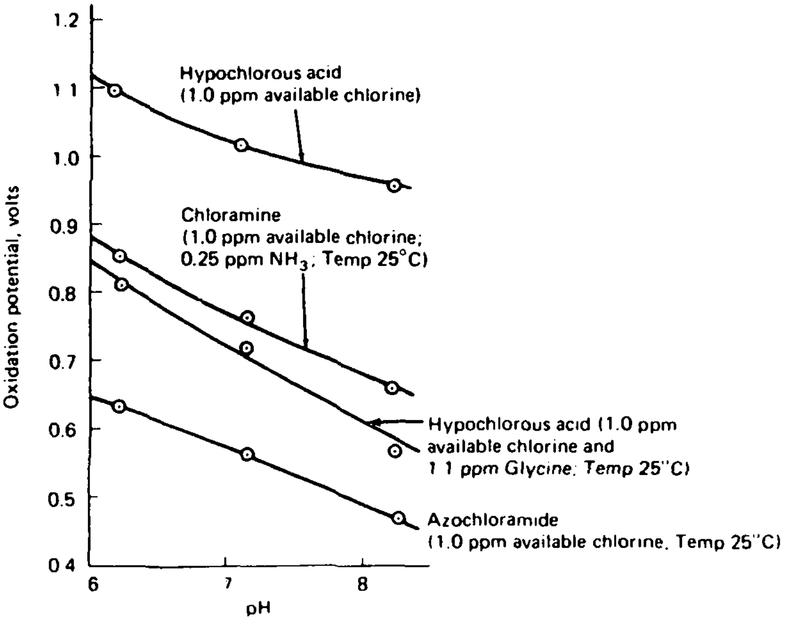

Fig. 4-14. Oxidation potentials of chlorine compounds.

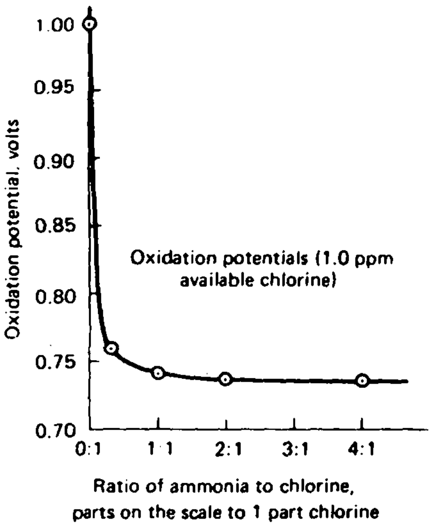

Fig. 4-15 Relationship of chlorine to ammonia ratio and oxidation potential.

early investigations it was generally believed that the germicidal efficiency of chloramines was less than free chlorine. Studies had suggested that the electrochemical properties of chlorine might be directly related to its germicidal efficiency.

In 1939 Schmelkes, Horning, and Campbell,[77] pursued this concept by investigating the "differential" potential of various types of free and combined chlorine residuals. Their work which confirmed the previous investigations is shown in Fig. 4-16. However they considered an additional variable described as the "base potential" of different waters. They found that raising the poise from 170 mV base potential to 190 mV might not produce the same germicidal efficiency as raising the poise in another water from 190 mV to 210 mV. Therefore, the degree to which a water was poised had a significant effect in evaluating the potential as related to germicidal efficiency. While this work left some doubt as to the reliability of the concept, it provided hope for future investigators.

In the next few years, S. L. Chang of Harvard University did some notable work on the destruction of microorganisms by chlorine.[55,56,78] Part of this work was an investigation of the oxidation potential concept of germicidally active chlorine.[79] Chang concluded that because of interfering substances, the uncertain amount of dissolved oxygen in raw waters, and the uncertainty of the reversibility of these systems, it was impossible to evaluate the potential measurements of residual chlorine. He did find that free chlorine, inorganic chloramines, and organic chloramines all had their own characteristic oxidation potentials but that the potential for one compound at cysticidal concentrations gives no information on the cysticidal efficiency of any other compound. This in itself renders this concept useless for evaluating the germicidal efficiency of different chlorine compounds.

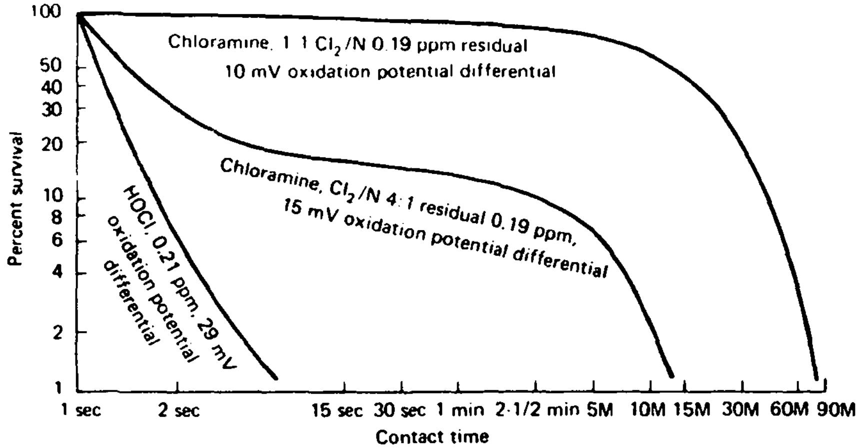

Fig. 4-16. Relationship of germicidal efficiency and oxidation potential differential.

## Practical Application of the ORP Concept

In spite of the inability to relate the ORP concept of chlorination to germicidal efficiency it has been tried in a variety of applications.

The practical value of ORP control of chlorination is in qualitative and not quantitative control. The foremost success of this method is in the destruction of cyanide wastes by chlorination. Here the operation depends upon the qualitative appearance of a chlorine residual that is clearly defined by plateaus in the ORP potential curve. The cyanide destruction process is not controlled by the amount of chlorine residual. (See Chapter 7.)

This method was thought to have great promise in the control of hydrogen sulfide odors in wastewater treatment processes. It has been tried over and over again without success. At present there is little or no interest in this application.

The ORP concept has been used successfully in the manufacture of hypochlorite solutions. This is a special case but must be mentioned here to avoid confusion on the subject.

The Diamond Shamrock Company developed a special electrode system that is made up of a single plastic rod containing a platinum measuring electrode and a silver electrode which becomes a silver–silver chloride half cell in the presence of a brine solution in contact with the silver electrode. This silver electrode develops a silver chloride coating due to the presence of high concentration of chloride ions. This half cell works well under these conditions as it is always in the same environment, i.e., a high concentration of same type of dissolved solids. The manufacture of hypochlorite by this electrode system, which is essentially an ORP system, is successfully accomplished because it is controlling to an alkalinity end-point by the addition of chlorine, not to an ORP value due to chlorine concentration.

ORP control of swimming pool chlorination has been used in the USA for at least ten years. The first successful system was developed by Frank Strand under the name of Stranco.[80,81] This system has proved so successful that other suppliers have entered the field. The system is made up of two parts: ORP control of the chlorine addition and ORP control of the *p*H. A control panel starts and stops the chlorinator and the *p*H control starts and stops a $NaCO_3$ chemical metering pump. The system maintains precise control of the *p*H which assures a constant percentage of undissociated HOCl. The ORP control maintains a high level of free chlorine (1.5–2.5 mg/l) which helps account for its success. A survey of three of these operating installations verifies their success and practicality for swimming

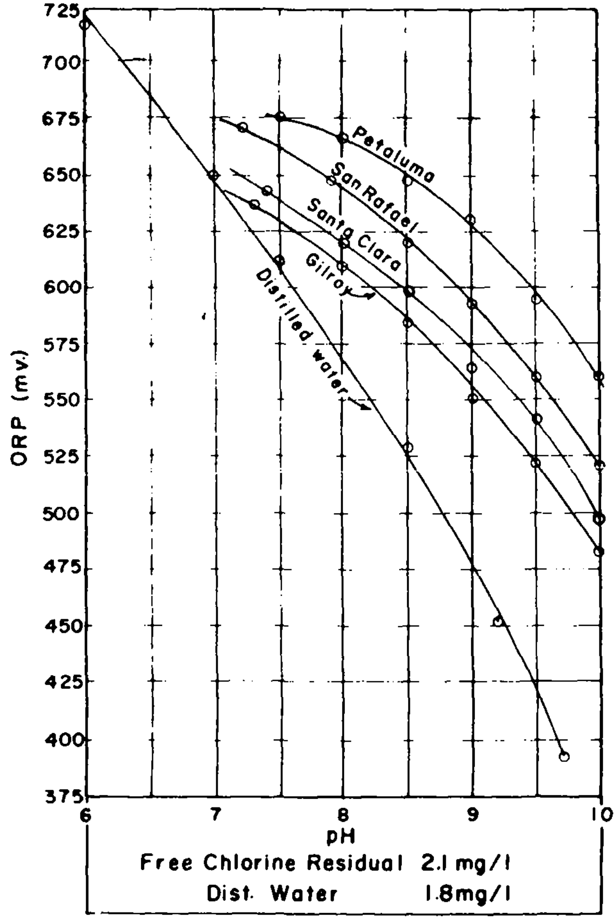

Fig. 4-17 Relationship between oxidation potential and pH at a fixed chlorine residual.

pool application (see below) In every case the Strantrol system, if with faults at all, errs on the side of safety The free chlorine residual was always in the 1.5–2.5 mg/l bracket and the pool water appeared brilliant and sparkling. At *p*H 7.5 this is an ideal situation.

In 1975 White investigated four swimming pools. Three of these pools were using the Strantrol system and one was using *p*H control and conventional chlorine residual control. The following relationships were investigated:

1. At a constant free chlorine residual of 2.1 mg/l, ORP measurements were made at *p*H levels from 6 to 10 (see Fig. 4-17). It is significant to note that the difference between the Gilroy and Petaluma waters is on the order of 60 mV for

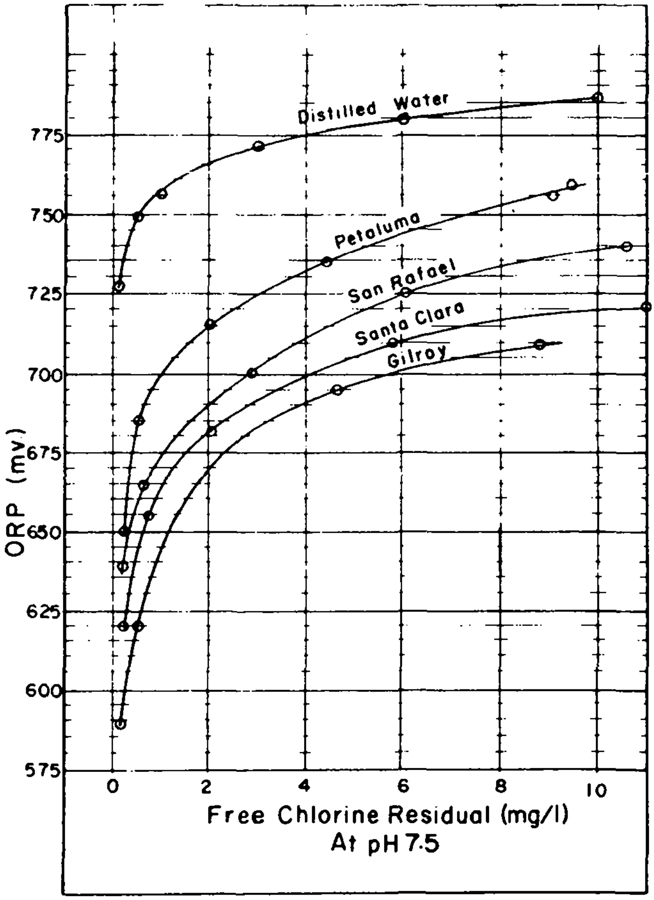

Fig. 4-18. Relationship between oxidation potential and free chlorine residual at a constant pH in five different waters.

identical *p*H levels These curves also show that any given water with a constant chlorine residual will show an ORP shift of about 60 mV when there is a one point shift in pH

2 With the *p*H constant at 7 5, ORP measurements were made with free residuals ranging from 0.1 to 10 mg/l (see Fig. 4-18). The curves shown demonstrate the logarithmic nature of the chlorine residual versus ORP values and the low sensitivity of this method of chlorine residual measurement. There is only 37 mV difference in the ORP values between 1 and 4 mg/l chlorine residual It is obvious that such a system will be inherently difficult to control. However there is another factor to be considered. A free chlorine residual tends to "poison" the ORP cell This reduces the sensitivity of the cell which retards the cell response to changes in chlorine residual and pH. In swimming pools where lag times may be long this can be a benefit.

Since the above investigation illustrates that every water has a different ORP "poise," each installation has to be calibrated to that poise. If the water source or the character of the water is changed a new calibration must be made This further demonstrates the fact that the ORP control method is qualitative and not quantitative. The success of this system is the close control of the pH and the maintenance of high free chlorine residuals. The close control of the pH insures the presence of a constant amount of undissociated HOCl which is the most active chlorine residual species.

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# 6

# Chlorination of Potable Water

## PURPOSE

Just as water is close to being a universal solvent, so chlorine is nearly a universal water treatment chemical.

The primary objective of water supply chlorination is disinfection. Because of chlorine's oxidizing powers, it has been found to serve other useful purposes in water treatment, such as taste and odor control, prevention of algal growths, maintaining clean filter media, removal of iron and manganese, destruction of hydrogen sulfide, color removal by bleaching of certain organic colors, maintenance of distribution system water quality by controlling slime growths, restoration and preservation of pipeline capacity, restoration of well capacity, main sterilization, and improved coagulation by activated silica.

None of the so-called alternatives to chlorine can compete with its versatility.

## HISTORICAL BACKGROUND

### Use as a Germicide

Chlorine was first introduced to water treatment as a disinfectant about the turn of the century. Since that time it has become by far the predominant method used for this purpose. This popularity is deserved because of its potency and range of effectiveness as a germicide. It is easy to apply, measure, and control; it is free from toxic or physiological effects; it persists reasonably well; and it is relatively inexpensive. Other agents may equal or even excel aqueous chlorine in any one of these characteristics, but there is none that combines them in such an advantageous way. Ozone, bromine, iodine, chlorine dioxide, silver ions, ultraviolet, and ultrasonics have been investigated. Some of these have found important uses in special situations, but none of them so far has been a serious competitor of chlorine.

As a result, of all the municipal water supplies that are being chemically disinfected, at least 99 percent use chlorine.[1] Very few processes enjoy this kind of monopoly. Even in countries where ozone is preferred, theoretically for physiological reasons, chlorination is almost universally employed in practice as an adjunct to ozone.

Probably the first known use of chlorine as a germicide was by Semmelweis, when in 1846 he introduced the scrubbing and cleansing of hands in chlorine water between contacts with each mother after he found that child bed fever (puerperal) was being transmitted from mother to mother in the maternity wards of the Vienna General Hospital. Then, in 1881 the German bacteriologist Koch demonstrated under controlled laboratory conditions that pure cultures of bacteria could be destroyed by hypochlorites. The earliest record of a suggestion to chlorinate water, even before water was known to be a carrier of disease germs, is a statement by Dr. Robley Dunlingsen in his *Human Health*, published in Philadelphia in 1835: "To make the water of the marshes potable, it has been proposed to add a small quantity of chlorine or one of the chlorides in small but sufficient amounts to destroy the foulness of the fluid."[2] Who originally made this proposal is not known. That water is a mode of transmission of disease has been known for only a little more than a hundred years. Dr. John Snow first theorized in 1849 that water was the mode of communication of cholera.[3] He was later able to demonstrate his theory in the Broad Street pump episode in London in 1854 by removing the pump handle, thereby staying an epidemic of cholera that had already claimed some five hundred lives. Dr. Snow also found the source of the infection: a soldier recently returned from active service in India, residing in a rooming house adjacent to the broken sewer which contaminated the water drawn from the Broad Street pump, was a carrier of cholera.[4]

## Early Uses in Water Treatment

The first use of chlorine as a continuous process in water treatment was probably in the small town of Middelkerke, Belgium, in 1902. This was known as the ferrochlor process. Ferric chloride for coagulation was mixed with calcium hypochlorite, which hydrolyzes to form a ferric hydroxide floc and hypochlorous acid as the disinfectant.[5] At Ostende, Belgium, in 1903, chlorine gas was generated by mixing potassium chlorate and oxalic acid. These installations, designed by Maurice Duyk, a chemist for the Belgian ministry of public works, are the earliest known continuous applications of chlorine for disinfection of potable water.

Chlorine in the form of hypochlorites (bleaching powder and chloride of lime) was first used as a temporary expedient to stay typhoid epidemics. The first recorded use was in 1896 when a typhoid epidemic occurred at the Austria-Hungary naval base of Pola on the Adriatic Sea.[2] In 1897 Sims Woodhead used a solution of bleaching powder for disinfecting Maidstone, England, water supply during a typhoid epidemic.[6] The first known continuous use of chlorine in England was at Lincoln in 1905.[7,8] A serious typhoid fever epidemic had occurred at Lincoln late in 1904, and was traced to the water supply. The advice of A. C. Houston, bacteriologist, and G. McGowan, chemist to the Royal Commission on Sewage Disposal, was sought. The source of the water supply was the River Witham and two small tributaries. Houston and McGowan recommended that the water be treated with chloros (alkaline solution of sodium hypochlorite of about 10 to 15 percent available chlorine), the most easily available chlorine compound at the time.[8] Treatment began on February 11, 1905, under the direction of D. B. Byles, starting with a dose of 10 ppm and finally settling on one of 1 ppm. The amount of water treated was 1 to 1½ mgd. This treatment continued until 1911, when a new supply of water came into use.

## First Uses in United States

The introduction of chlorination in the United States occurred on May 22, 1888, when patents on electrolytic treatment of water were issued to Albert R. Leeds, Professor of Chemistry at Stevens Institute of Technology at Hoboken, N.J.[2] Webster's British patent of January 27, 1887, was the forerunner and possibly the model of later patents issued in Great Britain and the United States for the use of electrode-generated current to disinfect potable water and wastewater. Leeds' theory of purifying water was to remove organic impurities found in natural waters or wastewaters which cannot be removed by mechanical filtration or chemical precipitation by treating the water with the gases obtained by the decomposition of water containing an acid or a salt in solution, the decomposition being effected by use of an electric current. The acid employed was to be either hydrochloric, nitric, phosphoric, chromic, or sulfuric, or the salts of these acids, or a mixture of these acids or salts. Leeds' thought that the best results would come from the hydrochloric acid, or its salt sodium chloride. So far as is known, Leeds did not follow up his patent with any operating installations.

Also in 1888 a patent was granted to Omar H. Jewell and his son William M. Jewell, both of Chicago, for a combination of electrodes with a mechanical filter. The patent was assigned to the Jewell Pure Water Company. The apparatus consisted of electrodes mounted vertically in the dome of a pressure sand filter. Passage of electric current through these electrodes and a solution of carbonic acid was supposed to produce an insoluble blanket of sodium bicarbonate on top of the filter sand to remove material that the sand could not. Nothing came of this device, which could not be demonstrated to be of any value.

Some years later William Jewell designed another electrolytic process which was used by George W. Fuller in January, 1896 for experimental work at Louisville, Kentucky. Twelve of Jewell's electrolytic generators were installed. These units required ten pounds of salt to produce one pound of chlorine. This installation was capable of providing a chlorine dosage of 0.25 mg/l into the filtered effluent. This same device was used again in 1899 on an experimental basis at Adrian, Michigan. Jewell experimented briefly with chlorine gas by this process but abandoned it in favor of chloride of lime.

In 1893 Albert E. Woolf used an electrolytic process, similar to the one used by Leeds, to generate chlorine in the sewage effluent at Brewster, New York. Disinfection was required here because the discharge was into the east branch of the Croton River, a part of the New York City water supply. This chlorination system operated successfully for 18 years, until it was destroyed by fire in 1911.

The first notable and successful chlorination installation in the United States is credited to George A. Johnson at the Bubbly Creek Filter Plant in Chicago in 1908, to serve the Chicago stockyards.[8-10] The raw water here contained a large amount of sewage and treatment consisted of filtration in conjunction with copper sulfate application. The large stock suppliers complained that animals drinking this water gained less weight than when city water was supplied to them.

Under pressure of a law suit brought by the city of Chicago against the Union Stockyard Company, the contractors who built the filter plant were enabled to fulfill their guarantee when Johnson substituted chloride of lime for the copper sulfate treatment. The rate of application was 45 pounds of chloride of lime (approximately 30 percent available chlorine) per mg seven and one-half hours before filtration. The treated water showed better bacteriological results than the city water: Bubbly Creek water showed 0.34 percent cases of *E. coli* versus 12.8 percent for city water.

## The Jersey City Case

Again in the same year, Johnson, who was a consulting engineer for the firm headed by George Fuller (Herring and Fuller), was hired by Dr. Leal to chlorinate the Jersey City water supply.[6,11] This installation is significant because it followed litigation over the quality of the new water supply. Jersey City had entered into a contract with the builders, who later identified themselves as the Jersey City Water Supply Company, to provide a new water supply. This work consisted mainly of constructing a large reservoir to impound water from the Rockaway River, a tributary of the Passaic, and a pipeline to carry 40 mgd of water from the reservoir at Boonton to Jersey City, twenty-three miles away. The contractors fell into financial difficulties, and the project had to be completed by the bonding company five years after the contract was awarded in 1899. Prior to its completion in 1904, Jersey City started a suit against the Jersey City Water Company, claiming that the work was not being performed according to the specifications, which read in part:

> The water to be furnished must be pure and wholesome for drinking and domestic purposes; and the works shall be so constructed and maintained by the contractor that the water delivered therefore shall be pure and wholesome and free from pollution deleterious for drinking and domestic purposes.

The city's claim was based on the pollution in the reservoir, which occurred two or three times a year during high water caused by storm runoff. The city claimed that the pollution could be corrected by a filtration plant. The defendants countered that if proper sewage disposal facilities were constructed by the city, this pollution would not occur.

The court rendered an opinion that the construction of a filter plant was not the responsibility of the defendants, and suggested, not as its own opinion but from evidence given by the city, that the water could be made to comply with the contract by the construction of sewers and sewage disposal works for various towns in the watershed.[6]

Dr. Leal was convinced that this would not entirely eliminate the pollution, and strongly advised that the company be allowed to suggest to the court its own method for the complete fulfillment of the contract requirements. He pointed out that the greater percentage of bacteria and *B. coli* found at the point of delivery in Jersey City was due primarily to the washing of soils, roads, streets, and manured fields rather than from any sewage contamination.

Leal's request was granted in a court decree filed June 4, 1908. Dr. Leal had in mind the electrolytic process of making chlorine, and on June 16, 1908, hired the firm of Herring and Fuller to build and operate a hypochlorite plant under the direction of G. A. Johnson. The plant itself was started on September 26, 1908. It was an enormous and cumbersome affair, as might be expected, consisting of three 10,500 gallon concrete chloride of lime solution storage tanks as well as a large building at the Boonton reservoir outlet.[11] After several months of operation, the dosage was reduced from approximately 1.0 to 0.2 ppm, requiring a high of 0.35 ppm during times of high water. Bacterial reduction in the raw material was from 200 to 20,000 per cc to from 20 to 30 per cc in the delivered water.

After several months of practical operation, extended testimony was taken in the court of chancery by ex-Chancellor Magie from a score of the foremost experts of that time. In his opinion, handed down in May, 1910,[11] Magie said:

> From the proofs taken before me, of the constant observations of the effect of this device, I am of the opinion and find that it is an effective process which destroys in the water the germs, the presence of which is deemed to indicate danger, including the pathogenic germs, so that the water after this treatment attains a purity much beyond that attained in water supplies of other municipalities. The reduction and practical elimination of such germs from the water was shown to be substantially continuous.

In the search for witnesses in this case, a toxicologist was sought to declare the process of chlorination a poisonous one. No one could be found who had this opinion.

It is interesting to note that the expert testimony developed the following theory of chlorination chemistry. Hypochlorous acid formed in the reaction of chloride of lime and water liberates oxygen in a very active state and leaves hydrochloric acid. The latter drives off the weaker carbonic acid and unites with calcium to form calcium chloride Hypochlorous acid will form whether or not the process is electrolytic production of molecular chlorine or hydrolysis of chloride of lime

However, the nascent oxygen theory of the killing action of chlorine presented in testimony in this case prevailed as the accepted theory until 1944, when it was finally disproved by S L Chang. (See Chapter 4.) The nascent theory was also responsible for the popularity of ozone.[5] Another point of interest developed was the fear of producing "free chlorine." This term referred to molecular chlorine and not hypochlorous acid, which is present-day terminology for free chlorine. This fear apparently stemmed from the knowledge of the toxicity of molecular chlorine, particularly in its contact with the respiratory tract of man.

The ruling by Magie in the Jersey City case gave chlorination a much needed boost but did not settle the argument as to the efficiency or desirability of chlorination as a water treatment process. There was a great deal of public sentiment as well as that of engineers against the idea of chlorination of potable water.[6,12] Many prominent persons in the water works industry proposed outright abandonment of a water supply source if it had to be disinfected, regardless of the method. These same persons were also against any kind of pollution, for which they must be commended. In the meantime, they gained considerable support from the public, who took great pride in a pure and wholesome water supply. This attitude was largely responsible for the revival of the Jersey City case some ten years after chlorination had been in successful operation.

In March, 1919, Jersey City, still irked by the two decisions against them in 1908 and 1910, appealed to the highest state court, the Court of Errors and Appeals, contending that chlorination does not afford the remedy claimed for it, asserting that in cold weather, "bacteria are stunned but not killed." Expert testimony and scientific evidence presented by the defendant clearly demonstrated to the court that chlorination was a reliable disinfectant that did in fact effectively destroy pathogenic organisms under all weather conditions.

Prior to the use of chlorine for disinfection and after the discovery of bacteria in water—thus making water as a carrier of disease—filtration was investigated as a practical means of mechanically removing these bacteria. This was accomplished at first by allowing the water to slowly settle through formations of specially graded sand, which trapped some of the bacteria but not all. Filtration became greatly improved by chemical precipitation and sedimentation prior to sand filtration. The first known use of a municipal filtration system was the one built in London in 1829.[11] The apparent success of the filtration system in Hamburg, Germany, during the 1892 cholera epidemic convinced sanitationists that filtration should be seriously considered as a treatment process for polluted water. Sand filter plants were built as early as 1874 at Poughkeepsie, New York. George Johnson, one of the outstanding proponents of chlorination for disinfection, stressed the inadequacy of filtration as the sole means of treatment for polluted water, and was able to amply demonstrate his opinions by scientific data collected at the Bubbly Creek filter plant in Chicago.[10,11]

Subsequent statistical evidence made public health experts aware of the necessity for establishing disinfection as a process either by itself or in conjunction with filtration or to abandon polluted supplies altogether. The statistics included data not only on death rates from typhoid fever but on the general community health.

## Typhoid Fever and Waterborne Outbreaks

The death rate from typhoid fever became a yardstick in the United States for public health authorities. Just before the turn of the century it was firmly established that this disease could be waterborne.

Military campaigns often produced virulent outbreaks. In the American Civil War, typhoid casualties were estimated at more than 75,000 cases, with more than 27,000 deaths. In the Franco-Prussian War, typhoid accounted for more than 73,000 cases, with more than 8,000 deaths; this latter death toll was higher than that from combat. The British suffered severe outbreaks in the Boer War, totaling more than 57,000 cases, with some 8,000 deaths.[13] A fateful individual case was that which took the life of Albert, Prince Consort to Queen Victoria in 1861.

The French and German armies adopted vigorous sanitation procedures as a result of their typhoid experience, so that on the eve of World War I the typhoid morbidity was down to eight cases per 100,000. It was in the Russo-Japanese War of 1904–5 that for the first time troops went to the front with units for boiling drinking water as a method of disinfection. By this time it had been established that boiling for a given length of time would kill the causative organism. In 1910 Whipple estimated that causes of typhoid fever could be grouped as: waterborne 40 percent; food 25 percent; ordinary contagion, including fly transmission 30 percent; shellfish and all others 5 percent.[5]

In 1900 the average death rate from typhoid in the United States was 36 per 100,000 population. Thus, more than 25,000 persons died of typhoid fever that year. The death rate dropped to twenty per 100,000 in 1910[13] and to three per 100,000 in 1935.[18] By 1960, less than twenty persons died from typhoid fever in the entire United States.[14]

Between 1920 and 1936, 470 waterborne outbreaks of typhoid fever in the United States and Canada caused nearly 1,200 deaths and illness to approximately 125,000 persons. During this same period, there were reported more than 16,000 cases of waterborne typhoid fever, more than 100,000 of gastroenteritis, more than 200 of bacillary dysentary, 1400 of amoebic dysentery, and 28 of jaundice. More than 30 percent of the United States outbreaks originated in well water. The cases of amoebic dysentery and jaundice were unique in water supply and public health history.[15]

The principal causes of these outbreaks, in order of magnitude, were: surface pollution of shallow wells; cross-connection with a polluted supply; contamination of spring or infiltration gallery by pollution of a watershed; contamination of a brook or stream by pollution on a watershed; use of polluted water from a river or irrigation ditch without treatment; inadequate chlorination as the only treatment; inadequate control over the filtration and chlorination process; seepage of surface water or sewage into a gravity conduit.

One of the most notable examples of chlorination of water supply for the safeguarding of public health is reflected in the efforts made by the Kansas State Health Department.[16] Between 1908 and 1917, at least thirty Kansas towns started using hypochlorite solutions for disinfection. In 1917, chlorine gas equipment was installed at Coffeyville and Valley Falls; by 1919, Atchison, Leavenworth, Herington, Independence, Iola, Kansas City, Ottawa, Sabetha, Topeka, and Wichita followed suit, by 1942, all sixty of the surface water supplies and forty of the ground water supplies in the state were so treated. Then in 1942, a disastrous waterborne bacillary dysentery epidemic of 3000 cases occurred in Newton, Kansas. Eventually, in 1956, the state health department ordered the chlorination of all public water supplies. By 1960, 462 of the 463 public supplies were being chlorinated.

Another factor of great importance in favor of safeguarding a water supply by chlorination was the tremendous cost to the cities in damages resulting from these waterborne epidemics. One example was the 1929 typhoid fever epidemic at Olean, New York, which cost the city $350,000.[15] Chlorination proved, among other things, to be cheap insurance.

### The Mills-Reincke Phenomenon and the Hazen Theorem

As early as 1893, two public health researchers, Mills and Reincke, discovered after studying a great many communities that when a polluted water supply was replaced by a pure supply, the general overall health of the community was greatly improved—to a greater degree than could be accounted for by the reduced prevalence of typhoid fever and other recognized typical waterborne diseases. This discovery became known as the Mills-Reincke phenomenon. In 1903, Allen Hazen, a pioneer in the water works industry, discovered that when a community water supply was changed from bad to excellent by adequate treatment, for every person saved from death by typhoid three other persons would be saved from death by other causes, many of which were probably never thought to have any connection with, or to be especially affected or influenced by, the quality of the public water supply. This change in the death rate was known as the Hazen theorem. Therefore, disinfection of public water supplies goes farther than just the control of waterborne diseases.

## WATERBORNE DISEASES

The sole purpose of disinfection of potable water is to destroy pathogenic organisms and thereby eliminate and prevent waterborne diseases. The following diseases are known to be transmitted by water, but not necessarily by water alone. Food and personal contact are other means by which these diseases may spread.

## Typhoid Fever

This disease was once a scourge that destroyed armies more effectively than weaponry and a pestilence that haunted towns because of its mystery. Typhoid masked itself in symptoms common to other ills and was often mistaken for typhus or was classified merely as one of many fevers. In North America it has been responsible for more sickness and death than any other waterborne disease. One frightening aspect is that the causative organism may be carried for a lifetime by an individual who has been infected but has recovered.* Not everyone who has contracted the disease and recovered becomes a carrier, but a great many do.

The causative organism of typhoid fever, *Salmonella typhi*, was discovered by Karl J. Eberth in 1880 (in some textbooks, it is referred to as *Eberthella typhosa*). This durable organism resides and proliferates solely in the intestines of man (not animals). It is readily destroyed by heat or such disinfectants as chlorine, iodine, bromine, and ozone. Under natural conditions in soil, water or feces, it can remain alive for weeks or months. Beard[19] confirmed that typhoid can survive up to five months in frozen debris and ice. When the ice was allowed to melt, the water became infected again.[19] Typhoid bacilli enter the body through the mouth, invade the mucosa of the small intestine, and traverse the intestinal lymphatic and mesenteric nodes to reach the blood. Subsequent proliferation occurs in the liver, gall bladder, biliary tract, and duodenum, with particular concentration in the lymphoid tissue of the small intestine mucosa. The bacillus is discharged in both the urine and feces, with stools becoming bacteriologically positive about two weeks after onset.

Since the organisms can retain their virulence and remain viable for long periods of time, any water supply contaminated by sewage is potentially a carrier of the disease if a carrier of the causative organism contributes to the sewage. Gradually over the years as the spread of this organism has been controlled by chlorination and other means of disinfection (boiling, iodine, ozone), the number of carriers

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* America's best-known typhoid carrier was Mary Mallon, otherwise known as Typhoid Mary, who came to symbolize a fearsome drama in the public mind. She worked as a cook for several upper-class New York families before being tracked down in 1907 as a carrier responsible for several outbreaks of the disease. When her feces were examined bacteriologically, it was found that she had practically a pure culture of the typhoid bacterium, *Salmonella typhi*. She remained a carrier for many years, probably because her gall bladder was infected and organisms were continuously being excreted from there into her intestine. She was imprisoned for 3 years when she refused to have her gall bladder removed. She was released from prison when health authorities accepted her pledge that she would not cook or handle food for others and that she would report to the health department every three months. She disappeared, changed her name, and cooked in hotels, restaurants, and sanitariums, leaving behind a wake of typhoid fever victims. After 5 years she was captured as a result of the investigation of an epidemic at a New York hospital. She was promptly arrested and imprisoned. She remained in prison for 23 years where she died in 1938, 32 years after she was discovered to be a typhoid carrier.[11,13]

has been diminished The incidence of typhoid in public water supplies is practically nil In 1981 the CDC in Atlanta, Georgia did not report a single case When a case is reported it is usually a foreign traveler Between 1946 and 1976, 610 cases were reported; 507 of these cases were traced to private water supply systems.[20] Continued diligence is necessary because the populace has not developed any natural resistance to *Salmonella typhi.*

Typhoid fever has put a strange blotch across the pages of history. It was a scourge that destroyed armies more effectively than weapons. This pestilence haunted towns because of its mystery. It masked itself in symptoms common to other illnesses. In the 19th Century mortality rates rose as high as 300 per 100,000. Military campaigns produced virulent outbreaks. In the American Civil War there were more than 27,000 deaths from typhoid, and in the Franco-Prussian War there were more than 8,000 deaths. The death toll in the latter war was more by typhoid than by gunfire.

## Cholera

Cholera was originally known as Cholera Morbus in its death-dealing form. It has been known in India since about 400 BC. The name was known the world over because of the magnitude of its attack rate which resulted in a high mortality rate. It ravaged entire cities. The organism stayed in India until 1817, when it escaped for the first time.[21] It spread at the leisurely pace of human travel in those times to China, Russia, Europe, and Britain. It took some 20 years to cross the Atlantic into North America. It came to Britain in 1831 and killed 21,000 people. There have been several epidemics in London caused by returning British soldiers who became carriers after contracting the disease while on military duty in India.[21]

In the 20th Century it has spread to the Philippines, Indonesia (Sulawesi province), the Middle Eastern countries, Africa, and Italy.

At one time cholera was common in Europe and North America, but the disease has been virtually eliminated in those areas by effective water treatment practices.

The causative organism was originally called *Vibrio comma* because of its shape. It is now labeled *Vibrio cholerae.* There is a new vicious strain of cholera organism, known as the El Tor *Vibrio.* It is slightly different from other strains. It is named after the Arab refugee camp in the Sinai Peninsula, which was hit by the disease in the 1960s. The El Tor cholera pandemic that reached Naples, Italy in 1973, began on the island of Sulawesi (Celebes) in 1960 and 1961. Then it turned up in the Philippines, and two years later in Korea, where it spread to China.

In 1981 there were 913 culture-confirmed cases of cholera El Tor, serotype Ogawa, which occurred in Bahrain. The overall attack rate was 27 per 10,000.[21] This outbreak was caused by drinking water. The Naples outbreak was caused by shellfish contaminated by sewage containing the El Tor organism.

Houston found in the 1930s that the virulence of *V. cholerae* is reduced 99 percent by one week's storage in water, and that the organism is easily killed by chlorine.[23]

The countries affected by cholera could easily wipe out this haunting scourge simply by practicing better hygiene, improved sanitation, and more effective water treatment practices.

### Amoebic Dysentery

Often referred to as amebiasis, this disease is a potential threat throughout the world. It is terrifying because it is almost impossible for a patient to experience complete recovery unless correct diagnosis and proper medical attention are immediately available. This disease was one of the most feared by our armed forces serving in the Pacific during World War II. The causative organism (*Entamoeba hystolytica*) is a cyst, and can therefore lie dormant in the intestinal tract and go undetected by the carrier for long periods of time, only to initiate a recurring illness without warning. The best protection against this disease is removal of the organism from water supplies by filtration. *E. histolytica* is large enough to be trapped by sand filters; high doses of chlorine (10 ppm) and a long contact time (one hour or more) are required to effect disinfection. One of the most notable of the several outbreaks of this disease in the United States was at the Congress Hotel in Chicago during the 1933 World's Fair, when the water system became contaminated with sewage through defective flushing valves on the toilet bowls. The most recent outbreak in the United States was in 1955.[25]

### Bacterial Gastroenteritis

There are sporadic outbreaks of this intestinal disorder which produces a wide variety of symptoms, such as nausea, vomiting, diarrhea, abdominal cramps, fever, and headache. The organisms usually responsible for such waterborne outbreaks belong mainly to four genera of organisms: *Shigella, Salmonella, Campylobacter,* and *Yersina.*

**Shigellosis.** The genus *Shigella* include *S. dysenteriae, S. paratyphi* (both responsible for paratyphoid in man), *S. shiga, S. sonnei,* and *S. flexneri.* The mode of transmission of these bacteria is by the fecal–oral route, which means they can be waterborne In the period 1946–1975 there were 49 outbreaks of shigellosis in the U.S.A which affected 10,869 people. The most common serotype isolated in these outbreaks was *S. sonnei.* The species *S. flexneri* has been isolated from patients following an outbreak on a cruise ship. This too was traced to the ship's water supply [26] This genus is also responsible for most foodborne outbreaks of gastroenteritis In general these bacteria are not long lived in the environment, so they are rarely isolated from bathing beaches or large bodies of water

**Salmonellosis.** Salmonellosis is the generic name of the diseases caused by organisms of the genus *Salmonella.* These organisms are most usually pathogenic to man and warm-blooded animals. The genus *Salmonella* contains over 1,000 distinct types having different antigenic specificities in their O antigens.

Until the Riverside, California outbreak in 1965, it was thought that *Salmonella typhi* (typhoid fever, described above), *Salmonella paratyphi,* and *S. schottmuelleri* (paratyphoid) were the only significant organisms of the genus *Salmonella* capable of carrying waterborne diseases. This outbreak was an epidemic of acute gastroenteritis that affected 18,000 people. There were three deaths. After a lengthy investigation it was concluded that the causative organism was *Salmonella typhimurium,* which was transported through the city water system.[27-29] The water supply was underground well water. Until this outbreak occurred it was generally believed that *Salmonella* species were only associated with food poisoning (excepting *S. typhi*).

The dominant organism in food poisoning is *S. enteriditis.* There are so very many strains of *Salmonella* that it is difficult to identify the particular strain in a foodborne outbreak that might be associated with a contaminated water supply. The CDC listed 18 foodborne *Salmonella* outbreaks affecting 1573 people in 1975 and a similar number of outbreaks in 1974 affecting 5499 people. The common factors in these outbreaks indicate that food prepared away from home has a potential for causing gastroenteritis.

**Toxigenic *E. coli.*** This bacterial pathogen has been found to cause travelers' diarrhea in Mexico, commonly called "Montezuma's Revenge." Median duration of the illness is about 5 days and occurs about 6 days after the travelers arrive in Mexico. There are, of course, other contributing pathogens such as *Shigella* and *Salmonella.* Enterotoxigenic *E. coli* has also been found to be responsible for diarrhea in travelers to Brazil and Kenya and in persons living in Brazil, Asia, Japan, and the U.S.[30] The World Health Organization believes that 80 percent of all intestinal illnesses in Third World countries is due to lack of sanitation and proper hygiene. The highest disease rate and death rate is from diarrhea, which is commonly waterborne.[31] The causative agent is most likely enterotoxigenic *E. coli.* In 1960 the diarrhea death rate in New York state was 2.4 per 100,000; in India it was 312 per 100,000.[31] Death from diarrhea is thought to be the result of dehydration. Other symptoms produced by this coliform pathogen include abdominal cramps, nausea, headache, vomiting, and fever.

In all cases investigated, the primary cause is either poor or no sanitation, absence of disinfection, malfunction of equipment, or improper design.

***Campylobacter* Enteritis.** Outbreaks of this disease have been reported as waterborne.[22,32] One in Sweden during October 1980 that affected about 2000 people was found to be caused by the species *C. jejuni.* This organism was isolated in the stools of patients. Neither food nor drink was found to be a common factor.

Epidemiologic evidence indicated that the infection was spread via the water mains, but the total coliform count gave no indication of fecal contamination.

The first outbreak of this disease occurred in 1978 in Bennington, Vermont. There were 3000 cases of diarrheal illness representing 19 percent of the population. Typical symptoms were abdominal cramps, diarrhea, and headache. The illnesses were associated with drinking water from the town water supply, which obtained unfiltered, but chlorinated, water from a nearby brook. *C. fetus* and *C. jejuni* were cultured from the feces of 42 percent of the cases, but not from 23 people who served as controls. Oddly enough, coliforms were not found in the water at the time of the outbreak. However, after chlorination dosage was increased and a boil-water order was issued, no further cases were reported. Another outbreak occurred in Britain at a boarding school, affecting 234 students and 23 staff members. The causative agent was again *C. jejuni*, which was traced to an unchlorinated water supply.

***Yersina* Enteritis.** An outbreak of gastroenteritis which affected 87 persons was reported from the state of Washington in January 1982.[32] An investigation identified *Y. enterocolitica* as the causative agent. The water supply used for the packing of soybean curd (tofu) was found to contain the causative organism. A water purification system which included disinfection was required to eliminate this health problem.

***Pseudomonas.*** *Pseudomonas aeruginosa* is considered to be an opportunistic pathogen. It is commonly found in water systems. It is primarily a soil organism, and frequently grows in filter systems. It has been known to cause gastroenteritis in newborn babies.[33] This "nonpathogenic" bacterium is a particular problem in hospitals, where infections are acquired from catheterizations, trachostomies, and intravenous intrusions. An epidemic of diarrhea in a hospital premature-baby nursery was traced to *Pseudomonas* bacteria in an aerating cap on a spigot used by ward personnel.[34,35] This raises an important point about the role of disinfection in water supplies. The advent of antibiotics has broadened or increased the range of conditions in which gram negative bacteria, such as *Pseudomonas*, may become pathogenic. Therefore the presence of these organisms in water supplies assumes greater importance than it has in the past because of the increased virulence of these organisms.

## Schistosomiasis

This serious parasitic disease is produced by a blood fluke, such as *Schistosoma mansoni*, which lives in human abdominal veins and expels eggs through the urine or feces. Within a few hours after discharge into fresh or brackish water, these ova mature into a free-swimming embryo known as *Miracidia* which escape the ova and then seek and penetrate a snail host. Within the tissues of the snail they grow and reproduce large numbers of larvae known as *Cercariae*. Literally thousands of these larvae emerge from a single snail each morning when the body of water in which the snail is living is warmed by the sun. The *Cercariae* are considerably larger than the *Miracidia*, can swim vigorously but not very far, but can be carried a long way by water currents. They tend to remain near the water surfaces, where they can easily make contact with swimmers or waders. Upon contact with human skin the *Cercariae* attach themselves by means of suckers and then start a process of penetration. Within hours they are in the blood stream and are carried to the liver, where they grow to maturity in a few weeks. They mate and move to small blood vessels in the walls of the intestine or bladder

It is estimated that this disease may affect some 200 million persons who live in tropical climates throughout the world.[36] It is thought that the disease can be contracted by drinking water contaminated with the *Cercariae*. This is a serious threat to public health because of the possibility of its being widespread by immigration of persons from areas where the disease is endemic. Once infected with the blood flukes, a victim never gets rid of the disease but finally succumbs after his vital organs are incapacitated. This cycle may take many years of gradual debilitation of the patient, who can function adequately most of the time and who is always a carrier of the potential infection to others. Chlorination appears to provide the most effective treatment of drinking and bathing water, but its application to streams or other uncontrolled waters is not practical.[38] Control may be best accomplished by breaking the life cycle of the *Schistosome* through environmental control, the principles of which include: preventing discharge of *Schistosome* ova into water courses; applying molluscicides to rid streams and ditches of snail hosts; killing the *Cercariae*; and protecting populations from contact with infected waters.[36,37]

## Giardia

The flagellated protozoan *Giardia lamblia* is responsible for the disease giardiasis in man. These parasitic flagellates are distributed worldwide and are the most commonly reported human intestinal parasites in the United States and Great Britain.[39,40] This is a debilitating febrile disease. The fever is accompanied by severe cramps, headache, and diarrhea. Children are more vulnerable than adults.[41] This organism has eight flagella and a ventral sucker which it attaches to the intestinal mucosa. This sucker causes diarrhea in the human species. Giardia cysts are carried by dogs, cats, and wildlife in addition to man. The disease has been referred to as "beaver fever" because it is thought to be spread by beavers who make their homes in the watershed. The primary source of *Giardia* infestation, however, is human feces. Giardiasis is found all over the world, primarily in places that have primitive hygienic practices and poor sanitary conditions. It is believed that leaking septic tanks and poorly treated sewage together with the proliferation of backpackers and campers has been responsible for the widespread outbreaks of giardiasis from coast to coast in the United States. People have passed it along by practices as diverse as having poor hygiene, participating in oral and anal sex or drinking polluted water [23]

In the years 1970–1980 outbreaks of giardiasis have tended to occur in small mountain communities in the Northeast, Pacific Northwest, and Rocky Mountains. However, in the 1980s larger communities have suffered outbreaks—Wilkes-Barre, Pennsylvania and Reno, Nevada.[23] More recently *Giardia* cysts have been found in the San Francisco water supply at the source. This is one of the highest quality waters in the U.S.A. It derives from melted snow high in the Sierra Nevada mountains adjacent to Yosemite National Park 185 miles east of San Francisco. This discovery is a stern warning that the natural barriers against transmission of waterborne diseases have finally been broken. This means that the pristine mountain water supply is a thing of the past and that disinfection of these supplies by current chlorination practices without coagulation, sedimentation, and filtration is no longer sufficient.

Inactivation by ultraviolet irradiation is not effective. Therefore UV is not an appropriate method of disinfection for Giardia cysts.[49]

*Giardia* cysts are extremely resistant to chlorine. Jarroll et al.[43] found that it required a chlorine concentration of 4 mg/l and a 60 min. contact time to kill all cysts in a chlorine-demand-free solution at *p*H levels of 6, 7, and 8.* This in effect means that in a system with chlorine demand the chlorine dosage would have to be sufficient to produce a 4 mg/l free residual at the end of 60 min. These findings compare favorably with those of Meyer and Jaroll.[40]

Giardia cysts are even more resistant to chloramines. This is to be expected, as they generally follow the disinfection resistance pattern of *Entamoeba* cysts. Bingham and Meyer[318] found that complete destruction of *Giardia* cysts required 4.5 hours contact time with 2.6 mg/l chloramine residual at a water temperature 50°F Sample water *p*H was not an important factor. Cyst death was slightly more rapid at *p*H 7.0 than at *p*H 8.5.

Inactivation of *Giardia* is best achieved by the multiple barrier approach. This would include removal of cysts by conventional water treatment processes such as flocculation, coagulation, sedimentation, and filtration. Any remaining cysts can then be inactivated by terminal disinfection. It is strongly recommended that prechlorination be applied as far upstream in the treatment train as is possible so as to achieve the optimum contact time of 60 min. This is similar to the recommendation for inactivation of *Entamoeba histolytica* cysts.

A chlorination system for a high quality surface water that does not require filtration can be designed to inactivate *Gardia* cysts, as has been done in some instances for amoeba cyst inactivation. In either case partial dechlorination after terminal disinfection must be considered.

## Legionnaire's Disease

Since 1977 the Center for Disease Control in Atlanta, Georgia has investigated 30 outbreaks of this disease.[44] A clear mode of transmission was not found. However, potable water as the basic source of the causative organism is strongly implicated in these and other investigations here and abroad.

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* At 5°C

The name of the disease derives from a mysterious explosive outbreak of pneumonia following an American Legion Convention in Philadelphia, Pennsylvania in 1976.[45,49] Pneumonia occurred primarily in persons attending the convention. Twenty-nine of the 182 cases were fatal. The causative pathogen was previously unknown in the annals of microbiology. The spread of the bacterium appeared to be airborne, but the source was not found. The epidemiologic analysis suggested that exposure may have occurred in the lobby of the headquarters hotel or in the area immediately surrounding the hotel.

Subsequent investigations of Legionnaire's disease at institutions have shown that multiple sites have yielded the causative agent, *Legionella pneumophila.* These include cooling towers, evaporative condensers, water heaters, faucets, and showerheads. Therefore it is highly probable that the source in the American Legion outbreak was the aerosols from the air conditioning system.

The earliest documented outbreak of Legionnaire's Disease occurred at St. Elizabeths Hospital (Washington, DC) in July and August 1965.[46] It was thought that this outbreak was in some way related to the excavation of the hospital grounds for the installation of a lawn sprinkler system. It was found that patients whose beds were near windows in buildings close to the excavation and patients who had access to the excavation were the ones who became ill. No attempt was made to recover the disease agent from the soil, which would have been most difficult at that time. However, in 1977 stored serum-pairs were tested and *L. pneumophila* were documented in 85 percent of the pairs. Since 1977, *L. pneumophila* has been discovered in mulch and soil.[46]

This disease is now known as legionellosis, which is the generic term for a group of diseases caused by the bacteria in the family *Legionellaceae,* genus *Legionella.* This family has one genus which contains at least six species: *L. pnuemophila, L. dumoffii, L. bozemanii, L. gormanii, L. micdadei,* and *L. longbeachii.* Although the species are genetically and antigentically distinct, they are morphologically and biochemically similar. *L. pneumophila* is the most commonly isolated species and has been found to have six serogroups.[46]

Legionellosis is currently recognized in two distinct forms: Legionnaire's disease, characterized by pneumonia with significant mortality rates; and Pontiac fever, which is a non-pneumonic, self-limiting febrile illness with a very high attack rate.[47] The incubation period for Legionnaire's disease is 2–20 days; for Pontiac fever it is only 5–66 hours.[48] Though the disease is respiratory in nature, person to person transmission has not been conclusively established. It is still not known why *L. pneumophila* causes two such different illnesses, or why the bacterium affects only 1 percent of the people exposed to it in the case of legionellosis, and as many as 95 percent in the case of Pontiac fever.[46]

It is paradoxical that an organism so fastidious in its nutritional requirements and so difficult to grow in the laboratory apparently persists and succeeds so well in an inanimate environment. The precise ecological niche and nutritional supply have not been defined.

*L. pneumophila* is now considered to be a common environmental contaminant.

It may be ubiquitous It has been isolated from many aquatic sites, including ponds, lakes, potable water, and equipment using potable water such as cooling water and evaporative condensers. *L. gormanii* has been isolated from a creek bank and *L. micdadei* has been isolated from nebulizer water.

The identification of legionella in 23 lakes in Georgia and 67 lakes (793 samples) in North Carolina, Florida, and Alabama[48] is cause for concern, although legionellosis does not occur by ingestion of water. It apparently attacks via the airborne route, as a result of aerosolization, and most likely utilizes algae or amoebae as transport mechanisms. Investigations have also demonstrated that *L. pneumophila* is able to colonize and grow in certain parts of water distribution systems. Warm water seems to enhance this ability. Legionellae have been found growing in certain species of free-living freshwater amoebae and soil amoebae. These amoebic species have been isolated from humidifiers, and if they are inhabitants of slime in showerheads, this could explain the presence of large numbers of *Legionellae* in samples from such fixtures. It has been estimated that a person inhaling a single infected amoeba could receive a dose of up to 1000 *Legionella* cells.[48]

It can be reasonably concluded that potable water probably is no more than the transport vehicle of this pathogen. However this can have serious implications because it tends to colonize and grow to high densities in components usually found in hotels and institutions. These components are storage tanks, cooling towers, evaporative condensers, showerheads, and water faucets.

*Legionellae* are susceptible to chlorination. Chlorination has been found to be effective at the 1-2 mg/l dosage level. Precise data for contact time and free residuals are not available. Institutions, hotels, etc., should make it a practice to sterilize their water systems on a regular basis similar to the recommended practice of main sterilization. This could be as frequently as once each six months.

Water suppliers whose systems have large holding reservoirs should be aware that *Legionellae* can work in such environments.

## Worms

Since the disease Schistosomiasis described above is carried by an organism sometimes referred to as a worm, it is pertinent to mention other worms that occur in water supplies. Free-living nematodes (NAIS), visible to the naked eye and resembling a tiny white worm, have been reported to occur in water supplies. In 1961 a survey of twenty-two cities indicate that these nematodes are fairly common in areas using surface waters. Although these nematodes are nonpathogenic, it is thought they might be able to ingest pathogenic organisms that could later transmit a waterborne disease.[50] Large numbers of one species, *Diplogaster medicapitus* of the Rhabitidae family, are present in the effluent of trickling filters and activated sludge process of sewage treatment and have been isolated in treated water supplies. They have been found to be capable of ingesting *Salmonella* and *Shigella* bacteria and Coxsackie virus Of the ingested pathogens, 6 to 16 percent survived one day and 0.1 to 1 percent survived two days. These nematodes resisted 2.5 to 3.0 ppm chlorine residuals in contacts of up to two hours. It is unlikely, however, that the nematodes could ingest pathogens at a sewage plant and be carried by the polluted water through the water system in one day. Even though the chance is remote, the threat exists.

While the problem of nematodes is primarily aesthetic, they can impart a strong earthy or musty odor to a water supply if allowed to propagate within the treatment plant. When the finished water shows more than ten worms per gallon, it should be investigated.

The most practical approach to preventing nematode infestation is to prechlorinate the raw water to a free residual of 0.5 ppm and six hours contact time. Although many of the nematodes will not be killed, they will be sufficiently affected so that they cannot survive and will therefore be settled out in the flocculation process.[50]

## Tularemia

This disease of rodents, man, and some domestic animals derives its name from Tulare County, California, where it was discovered. In man it produces an irregular fever which continues for several weeks and results in moderate to severe debilitation.

The usual means of transmission is by direct contact, although the causative organism *Pasteurella tularensis* has been isolated in certain streams in Montana that are sources of water supplies.[51] These organisms are easily destroyed by chlorination.

## Acute Gastrointestinal Illnesses (AGI)

All reported outbreaks of unknown etiology are classified by the CDC and EPA as AGI. In the period 1971 to 1977 a total of 192 outbreaks of waterborne disease affecting 36,757 persons was reported in the U.S. There was no etiology in 57 percent of the outbreaks and 58 percent of the illnesses.[68] These illnesses are therefore listed as AGI. Before the cooperative effort between the CDC and EPA to document, investigate, and report waterborne outbreaks in 1971, AGI outbreaks were not always documented. For example, in the 10 year period 1961–1970, of 130 waterborne outbreaks affecting 46,374 people, 30 percent were classified as a gastrointestinal outbreak of unknown origin.[20,69] In 1981, 44 percent of the outbreaks, affecting 43 percent of the cases, were classified as AGI in the CDC Annual Summary.

## Recently Described Conditions with Conspicuous GI Symptoms

At a 1983 gastroenterology seminar held in London,[297] several important new microbial agents and infective conditions were discussed as to the clinical features,

## Table 6-1 Recently Described Conditions with Prominent Gastrointestinal Symptoms

| *Syndrome* | *Causative Organisms* | *Site of Infection* | *Main Gut Symptoms* |
|---|---|---|---|
| Toxic shock syndrome | *Staphylococcus aureus*—enterotoxin F-producing strains | Vaginal and other sites | Diarrhea |
| Legionnaire's disease | *Legionella pneumophila* | Lower respiratory tract | Diarrhea and vomiting; abdominal distension |
| Traveller's diarrhea | *E. coli*—enterotoxigenic strains; *Campylobacter* spp. | Gut | Diarrhea |
| Gay-bowel syndrome | *Giardia lamblia Entamoeba histolytica* | Gut | Diarrhea |
| Infant botulism | *Clostridium botulinum* | Gut (?) | Constipation |

pathogenesis, epidemiology, occurrence and infection site. These recent syndromes are listed in Table 6-1.

The gay-bowel syndrome is of interest in this text because the causative organisms *Giardia lambia* and *Entamoeba histolytica* are waterborne diseases. This syndrome refers to sexually active homosexual males. Whether or not the persons suffering from this malaise are potential carriers is not known. It is well known, however, that the causative organisms are virulent and difficult to destroy. Since this situation involves the fecal-oral route of transmission, foodborne infections are possible.

A 1982 survey of a large sector of the San Francisco gay community was made by a medical task force from the Kaiser-Permanente Medical Center.[298,299] This survey studied the intestinal parasitic infections in homosexual males and found, among other things, that 68 percent had intestinal parasites (*G. lamblia* and *E. histolytica*). This finding compares with a national background level of about 3 percent. This should be of concern to those involved in water production and food handling.

## Viral Diseases

**General Background.** All viral diseases are not waterborne. The human enteric viruses (poliomyelitis, Coxsackie, and echo) do not produce their associated diseases via the waterborne route.[52] It is also possible to have these viruses in the blood stream without having the disease. These facts appear to contradict the nature of the diseases involved, which complicates the understanding of viral diseases, especially in potable water supply.

Adenovirus, which is not an enteric virus, has been reported to have caused a disease outbreak in a water supply.[53]

The viruses of known concern to potable water producers are: Hepatitis A, Norwalk, and Rotavirus. It has been said that the latter two are responsible for about 77 percent of acute waterborne gastroenteritis.[54] These three viruses can and do travel the waterborne route. It is claimed by some investigators that Rotavirus can survive modern wastewater treatment processes. These viruses travel the fecal–oral route.

**Coping with Viruses in Potable Water.** It is the consensus of virologists that the raw water of all surface water supplies in the U.S.A. and Canada contains naturally occurring human enteroviruses. These investigators and public health agencies believe that it is necessary to adopt the multiple barrier approach in order to protect the public from sickness attributable to viruses.

A comprehensive study by O'Connor et al., published in 1982,[55] concluded that virus removal and inactivation are essentially complete when modern treatment practices are followed. This means the use of prechlorination, flocculation, coagulation, sedimentation, and filtration followed by terminal disinfection. Prechlorination will enhance the reliability of the treatment plant to remove and inactivate the viruses because of the extended contact time through the treatment processes. If the coagulation step is to be effective the water must have a reasonable amount of turbidity.

In those instances where riverbank filtration is used to simulate slow-sand filtration, flooding the banks will nullify the purpose of this treatment step and cause a rapid increase in the virus concentration in the treatment plant.

Another situation which causes virus population increase is sludge blanket breakthrough in the sedimentation step.

The effect of chlorination system failures is well known and need not be repeated here.

Another promising method of virus removal is by storage. For this method to be effective, the water to be stored must be biologically active. Virus removal by storage can easily achieve levels of one plaque-forming-unit.[53] Storage is reliable if there is no short circuiting. The use of lagoons has been studied in Israel for many years. Three log reductions of viruses in wastewater after 28 days storage have been observed.[56]

If every effort is made to remove or destroy all viruses in potable water it seems unrealistic to set zero virus count as a goal.

**Consensus Organism Indicator.** It is not possible at this time to isolate an organism that would serve as a virus indicator. Moreover, the problem is compounded by the fact that there is no observed relation between the microbial indicators, such as total coliforms, fecal coliforms, or standard plate counts, and the presence of viruses. Also there is no observed relation between the detection of *Salmonellae* and viruses and vice-versa. Nor can the enteroviruses or coliphages be used as virus indicators with our present knowledge of the organisms.

For example, a potable water could be contaminated by a small source which introduces viruses but no fecal indicators like total or fecal coliforms. Likewise, if there is a fecal contamination from a populace which is not "shedding" the virus there would be fecal indicators but no viruses.

**Adenoviruses.** These viruses, originally isolated from tissue culture of human adenoids, are responsible for febrile pharyngitis, swimming pool conjunctivitis, and acute respiratory catarrh. They are not enteric viruses but apparently can be waterborne, as they have been detected in surface waters. There are some 28 serologic types of this group of viruses. Types 4 and 7 are found in most cases of acute respiratory disease. Types 1, 2, and 5 are frequently associated with febrile respiratory infections in young children. Types 6 and 10 cause conjunctivitis, which can be transmitted in swimming pools and possibly other surface waters. It is common in recruit camps where attack rates have been reported as high as 70 percent. It is also seen in children's institutions due to the crowding together of susceptible young hosts.[57] While these viruses are resistant to antibiotics[41] they are the most susceptible to chlorination of all the viruses normally detected in surface waters.

**Enteroviruses.** These viruses derive their name from the fact that the alimentary tract forms a reservoir where they may be found. They enter the body through the mouth. Infection is spread mainly by the fecal–oral route caused by poor hygiene, poor sanitation, or a poor-quality water supply. These viruses cause the greatest concern in water supply practice because of the severity of the diseases they carry as well as their resistance to disinfection. The enteric viruses of least concern to the water producer are the poliomyelitis, coxsackie, and echoviruses, for reasons described above. These are not considered to be waterborne, in spite of the fact that they are excreted in the feces of infected patients.

*Poliovirus.* This virus is the cause of what used to be a common infectious disease of the central nervous system known as infantile paralysis, or poliomyelitis. The virus was thought at one time to have been transmitted by water supplies because it is readily detected in the feces of infected patients. However, a great many studies have failed to confirm this theory. The introduction of mass vaccination in the United States about 1960 has reduced the occurrence of poliomyelitis to something less than 5 cases per 100,000 per year. It appears that permanent immunity may be possible provided booster doses are taken at specified intervals. Therefore it is practically impossible to prove whether or not the disease is waterborne without the occurrence of an epidemic.

*Coxsackie.* This virus is so called because it was first isolated at Coxsackie, New York. There are many types of this virus which cause Bornholm disease, named after a Danish island in the Baltic Sea, where there was an epidemic of pleurodynia (an inflammation of fibrous tissue causing acute pain in the side), herpangina (a contagious disease of children characterized by fever, headache, and vesicular eruption in the throat), and epidemic pharyngitis. Some types of Coxsackie viruses are the most resistant of all viruses to chlorination. Here again this is of no concern, because the diseases caused by this virus are not known to be waterborne.

*Echoviruses (Enteric, Cytopathogenic, Human Orphan).* These are so called because on first isolation they appeared to be associated with no known human infection. They have since been shown to cause acute respiratory symptoms, enteritis, and meningitis.[58] There are more than twenty different types.

*Infectious Hepatitis (Hepatitis A).* The etiological agent is a virus whose characteristics are not yet completely known. Another type, serum hepatitis, is clinically indistinguishable from infectious hepatitis, although the virus is different. Infectious hepatitis is an acute viral inflammation of the liver characterized by fever, malaise, gastrointestinal symptoms (nausea and vomiting), and jaundice. The fact that infectious hepatitis can be waterborne is well documented. Its incidence has been rising to such an alarming extent since about 1950 that it is recognized as a disease of considerable environmental significance and one which is of great concern in water supply practice. The most explosive and devastating waterborne outbreak of infectious hepatitis occurred in New Delhi, India, in 1955–56, resulting in more than 50,000 cases.[59] The raw water was known to have been contaminated by domestic sewage, but the water was treated by conventional methods. The failure of the treatment process was traced to an inadequate chlorination facility.

## Viral Gastroenteritis

*AGI.* This is the label for acute gastrointestinal illness of unknown etiology. CDC reported 4,430 cases of waterborne illness from 32 outbreaks for the calendar year 1981. AGI accounted for 1893 cases from 14 outbreaks, while Rotavirus accounted for 1761 cases from only one outbreak. It is speculated that the majority of AGI cases are the result of Norwalk-like viruses.

*Norwalk Virus.* This virus has been associated with epidemics of acute gastrointestinal illness occurring in families, schools, and communities.[60–62] It is regarded as a common pathogen of older children and adults in the United States. This is an interesting observation, because the original outbreak caused by this virus occurred in an elementary school in Norwalk, Ohio, October 30–31, 1968. Its role in pediatric diarrhea has not been thoroughly investigated. The incubation period is 18–48 hours, and symptoms last from 24 to 48 hours. Usual symptoms are abdominal cramps, headache, malaise, low grade fever, nausea, and either vomiting or diarrhea or both. This sickness has often been characterized as 24-hour flu.[60,62,63]

An investigation of 25 separate outbreaks of nonbacterial gastrointestinal illnesses were studied serologically for evidence of infection with the Norwalk virus and the rotaviruses. Eight of the 25 appeared to be related to the Norwalk virus. In one of the 25 there was evidence of Rotavirus infection. These observations suggest that the Norwalk virus or serologically related agents play an important role in epidemic nonbacterial gastroenteritis in adults and older children.[62,63]

The outbreaks studied occurred in communities, cruise ships, schools, summer camps, and colleges. The 1968 Norwalk outbreak was studied by means of stool swabs. These swabs failed to detect *Salmonella, Shigella,* enteropathogenic *E. coli, Staphylococcus aureus, Aeromonas,* noncholera *Vibrio,* or enterococci. The attack rate was 50 percent (116 of 232) of students and teachers. There were several schools in the town, and food for lunches was distributed to all schools. There was no illness at any of the other schools. It was concluded that the source was the water well at the affected school, which was the only school that had its own well.[64]

In August 1980 there was a potable water-related outbreak of acute gastrointestinal illness in the community of Lindale, Georgia.[65] The attack rate was determined in 10 neighborhoods. This rate increased significantly near a textile plant where there was known to be a cross-connection between an industrial water supply system (which contained fecal coliforms) and the community potable water system. The infectious agent was thought to be waterborne. There is ever-increasing evidence that acute gastrointestinal illness is indeed waterborne and one of the more important infectious agents is Norwalk virus.[66]

*Rotavirus.* This virus is known to cause both sporadic and epidemic cases of gastroenteritis in infant and young children throughout the world. Approximately one-half the infants and young children hospitalized with diarrhea are infected with rotavirus. In temperate climates the peak prevalence is in the winter months. Infection is uncommon in the summer. Transmission is thought to be by the fecal–oral route. Diarrhea of 5–8 days' duration is the main feature of rotaviral disease. It is frequently accompanied by vomiting and fever. Death due to this virus is rare but has been reported. Rotaviruses have been observed in diarrheal feces from the young of numerous mammalian species.[60] Waterborne rotavirus infection has been reported in Europe.[57,67] This virus is not believed to be as important as the Norwalk virus as the cause of acute gastrointestinal illness (AGI).

## Summary

Examination of the statistics tends to indicate that waterborne outbreaks are on the upswing. This may be due to better reporting or it may be that some of the barriers are being overstressed. Public health agencies are deeply committed to the theory of multiple barriers or multiple points of control between sewage discharges and water supply intake. These barriers or points of control include wastewater treatment, land confinement, dilution, time, distance, and potable water treatment. Any type of treatment is fallable, so reliance on natural barriers should be maintained as long as possible. However, it is obvious that disinfection of potable water is the last line of defense.

The Safe Drinking Water Act of December 1974 resulted in improved surveillance of drinking water supplies. The provisions of this act apply to all water systems serving 15 connections or at least 25 individuals for a minimum duration of 60 days. This act was followed by the National Interim Primary Drinking Water Regulations created by the EPA in 1975 and implemented in 1977. These regulations established maximum contaminant levels for specified microbiological and chemical contamination, as well as turbidity limits and monitoring frequency.

A perusal of the annual reports by Gunther F. Craun in the *J. WPCF* June issue, Literature Review, under the heading "Disease Outbreaks Caused by Drinking Water," 1971–1980, reveals some interesting data about the supplies involved in these outbreaks.

The supplies that suffered the most outbreaks were the noncommunity supplies such as cruise ships, resorts, summer camps, boarding schools, and other small private supplies. In one year these supplies accounted for as much as 75 percent of the outbreaks. However it is the community supplies that account for the greatest number of cases, about 85 percent of cases each year. The traveling public suffers greatly from waterborne illnesses, particularly in Mexico.

The causes of these outbreaks fall into the following categories: contaminated ground water—65 percent of outbreaks and 63 percent of cases; inadequate or interrupted chlorination, 31 percent of outbreaks and 44 percent of cases. In some years contamination of the municipal distribution system causes as much as 70 percent of cases.

It remains to be seen whether or not waterborne diseases are on the upswing. It may be that the reporting is more comprehensive.

## EARLY DEVELOPMENT OF CHLORINATION EQUIPMENT

### Historical Background

The next important development in the progress of chlorination was the invention of apparatus that could use chlorine gas directly from a cylinder. Until about 1910 the only successful practical method was using hypochlorite solution. The one successful electrolytic installation at Brewster, New York, which operated continuously for eighteen years on sewage effluent, was replaced by a hypochlorite installation after the original one was destroyed by fire in 1911. At best the hypochlorite method was cumbersome, extremely awkward, and messy to handle and apply. In June, 1910, C. R. Darnall, a major in the Medical Corps, U.S. Army, began to experiment with liquid molecular chlorine compressed in steel cylinders.[17] The cylinders, which were not then available in the United States, had to be shipped here from Germany. Major Darnall not only made the first practical chlorinator using chlorine gas,[18] but also published the first work on the bactericidal efficiency of elemental chlorine dissolved in water [17,70] Darnall's apparatus (U.S. Patent 1,007,647), illustrated in Fig. 6-1 consisted of a pressure-reducing mechanism, a metering device, and an absorption chamber Only one of these units was ever installed- -at Youngstown, Ohio.

Although Darnall never entered into the equipment field, he intended to set up license agreements with communities to install his equipment for waste disinfection. Under such an arrangement, the community would pay him a royalty based on per capita per year or total amount of water treated. He approached the Electro Bleach Gas Company of Niagara Falls, New York, which in 1909 was one of the first commercial producers of liquid chlorine in the United States, and proposed that all the liquid chlorine used in his installations be supplied by the company and that, in return, the company should agree to sell liquid chlorine for this purpose to no one else. E. D. Kingsley, president and founder of the company agreed, provided that Darnall furnish the chlorine feeding device in working form within six months. When Darnall failed to do so, Kingsley assigned the job of developing such a device to George Ornstein, then a consulting chemist to the company, employed to develop applications for liquid chlorine in bleaching textiles and paper pulp.[38]

Meanwhile, in December, 1912, John Kienle, chief engineer of the Wilmington, Delaware, water department, began experimenting with the application of chlorine gas from cylinders.[70] He fed the chlorine gas to an absorption tower, through which a counter flow of water absorbed the chlorine, which was then applied as an aqueous solution. A balanced, weighted pressure-reducing valve was connected to the cylinder for chlorine feed-rate control but became inoperative and so was discarded; only the valve on the cylinder was available for control. Kienle recommended to his water board that installation of such chlorination equipment be made, but only by a manufacturer that agreed to demonstrate efficiency of control for thirty days and guarantee the apparatus against deterioration for one year.

Following Kienle's experiments at Wilmington, Ornstein developed a chlorine control apparatus (U.S. Patent 1,142,361) which consisted of a high- and a low-pressure gage, the latter being calibrated to indicate the flow of gas through a fixed orifice. The metered gas was then directed into a stoneware absorption tower, where it became dissolved in the water flowing by gravity out of the bottom of the tower as an aqueous chlorine solution. This unit was first tested on a plant scale in November, 1912, at the Western New York Water Company plant at Niagara Falls. Under the direction of Harry F. Huy, the bacteriological results using this apparatus were documented and compared with the chloride of lime method.[38] The results exceeded expectations. This experimental apparatus was greatly improved, and on February 1, 1913, the Ornstein chlorinator, as manufactured by the Electro Bleach Gas Company, was put into operation at Kienle's Wilmington, Delaware, plant This is considered the first commercial solution feed chlorinator installation in the United States [18,38] John Kienle shortly thereafter

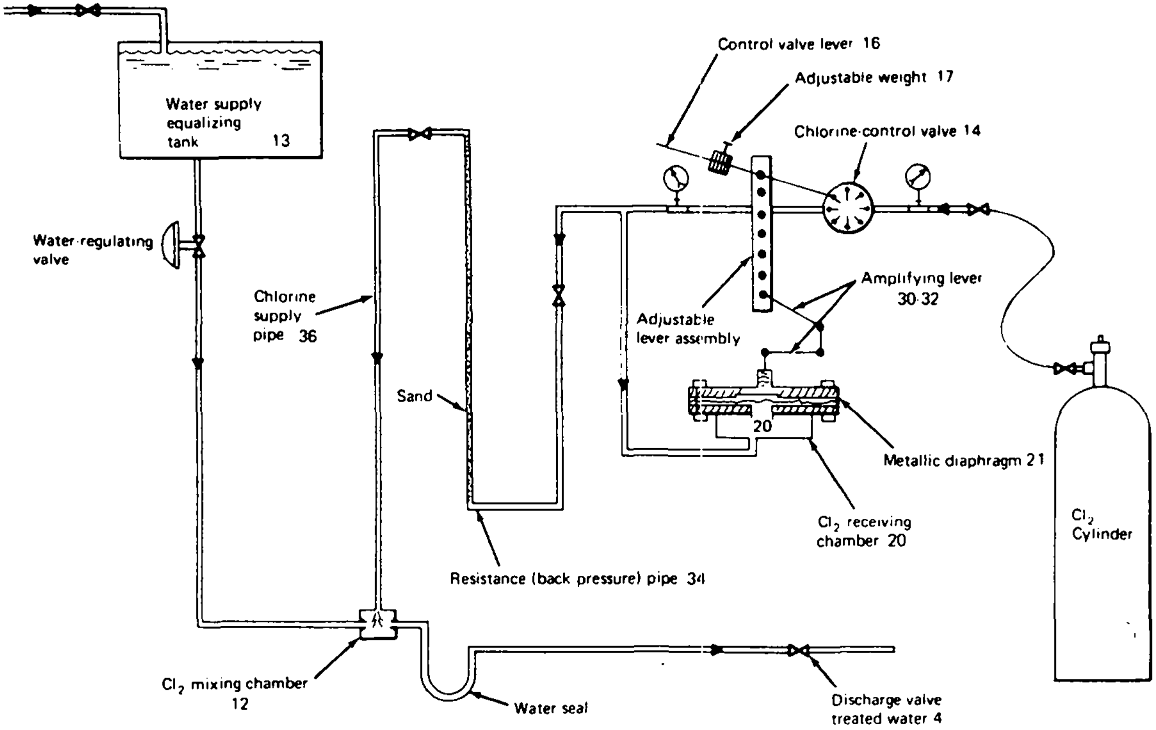

Fig 6-1 Major Darnall's chlorinator. When valve on chlorine cylinder is opened the chlorine gas passes through piping and control valve to the receiver 20 in the diaphragm-type chlorine pressure-reducing valve and simultaneously through the back-pressure assembly 34. Because of the pressure buildup in 34, the pressure in 20 rises and lifts the metallic diaphragm 21, which operates the lever assembly 30–32 so as to close the chlorine control valve 14. As the gas passes through chamber 34, the pressure in chamber 20 falls and the lever assembly 30–32 operates to open valve 14, thus permitting more gas to pass.

The quantity of chlorine may be increased or decreased by shifting weight 17 on lever 16. Once adjusted, the chlorine flow is presumed uniform. The water flow is maintained constant by means of the equalizing tank 13.

Supposedly this system was meant to be automatic start-and-stop based on opening and closing valve 4 as follows:

If valve 4 is closed, the flow of water out of the tank will stop and presumably raise the pressure in pipe 34 via pipe 36, thereby reacting on the chlorine diaphragm assembly 21, causing the flow of chlorine through valve 14 to shut off.

became associated with the Electro Beach Gas Company to manage the sales of its chlorine feeding equipment. Under his guidance, installations of this equipment were made in both potable water and wastewater plants, as far west as Salt Lake City, Utah, Monterey, California, and Seattle, Washington.

About this time, Wallace and Tiernan entered the field. The firm set about making a gas chlorinator for an installation at Dover, Delaware, on the Rockaway River, a tributary which fed the Boonton, New Jersey, reservoir. This, their first direct-feed gas chlorinator, was installed February 22, 1913.[18] This installation included a gas pressure gage, a temperature-pressure compensating device, and an ingenious inverted glass siphon for measuring low rates of chlorine gas flow which is still in use today in modern equipment. The chlorine gas was applied directly to the water being treated, where it was dissolved by means of porous ceramic diffusers. This new chlorinator was simple and dependable in operation, and so it soon gained popular acceptance. Late in 1913, Wallace & Tiernan began developing solution-feed chlorinators, which proved more reliable than the direct-feed units. The direct-feed gas diffusers were plagued by cold weather. Within a year, Wallace and Tiernan began to dominate the field. By September, 1914, they had twenty-three chlorinators installed in eighteen different cities; in 1916 they installed nine direct-feed units in Croton, New York, aqueducts. In 1917, Wallace and Tiernan became sole licensee of the Ornstein patent and the Electro Bleach Gas Company discontinued marketing its liquid chlorine feeding equipment. By 1918, Wallace & Tiernan equipment was installed as far west as California; by 1920, they were represented by sales and service facilities in major cities throughout the United States; and in 1925 the British company was established. After World War II the company was represented around the world; its impact on the water works industry was extraordinary. In the late 1920s, when it was confirmed that a combination of chlorine and ammonia could eliminate many tastes and odors due to chlorination, Wallace and Tiernan promptly supplied the appropriate metering and control equipment to handle anhydrous ammonia.

In the years that followed, the name Wallace and Tiernan became synonymous with chlorination. They were responsible for all the significant developments in chlorination apparatus. Among these achievements were: the unique vacuum solution-feed chlorinator utilizing the aspirator-type injector; the development of the visible vacuum principle of equipment (cà 1920), which resulted in an industry-wide change in the manufacturing of chlorine gas to produce a cleaner, less troublesome product. Fig. 6-2 is an illustration of the bell-jar chlorinator, invented by C. F. Wallace. This particular model (A-255) was the first automatic flow-paced solution-feed chlorinator (ca 1925).

This was followed by the development of the amperometric titrator in 1942 by Henry Marks of Wallace and Tiernan. This invention provided the analytical techniques required for the control of the free residual process in accordance with the breakpoint phenomenon. Shortly thereafter the continuous amperometric chlo-

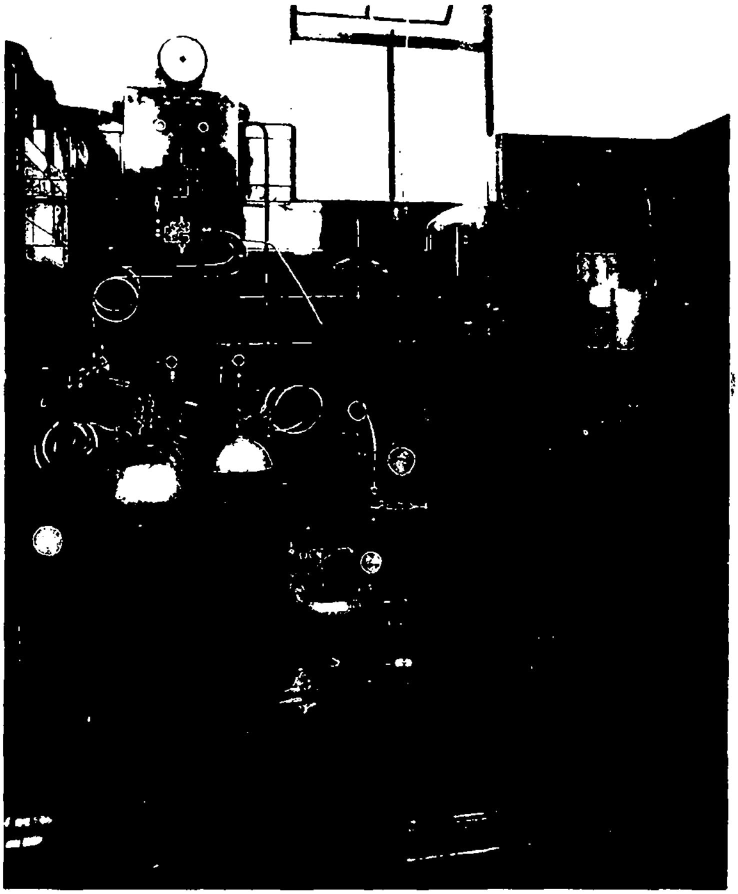

Fig 6-2 Flow paced automatic bell-jar chlorinator Wallace and Tiernan Series A-255 (courtesy Wallace and Tiernan Div Pennwalt, England).

rine residual analyzer was made available (ca 1950), followed in 1953 by apparatus capable of automatic residual control. Other significant developments were: the first chlorine leak detector (ca 1955) and the compound-loop principle of automatic chlorine residual control (U.S. Patent 2,929,393) introduced in 1960.

In the early days of chlorination (1920s) Wallace and Tiernan devoted a considerable amount of time to residual control research. Systems were developed which could continuously control to a specific O-T residual. The first of these was installed at Little Falls, NJ in 1929; the second at Rahway, NJ, in 1930.[71] A modification of these units was installed in 1932 and 1934 on the Los Angeles System.[72] The Lower San Fernando installation is shown in Fig. 6-3.

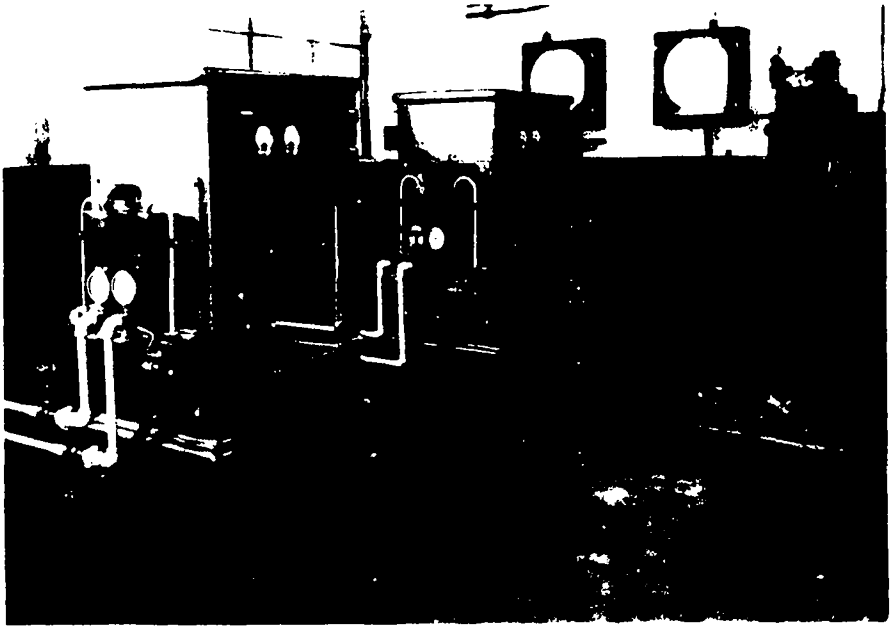

Fig 6-3 Colorimetric chlorine residual controller lower San Fernando. Reservoir Los Angeles Department of Water and Power (courtesy Wallace and Tiernan Div Pennwalt).

## Advances in Equipment

During these early years the most successful competitors of Wallace and Tiernan were Pardee and Everson Manufacturing. Wallace and Tiernan controlled about 90 percent of the chlorinator business until Fischer and Porter entered the field in the early 1950s At that time plastic pipe and fittings were beginning to replace rubber hose and rubber-lined pipe for chlorine solutions. The use of injection-molded plastic components transformed the manufacturing concepts of chlorinators overnight. Fischer and Porter capitalized on these developments. They displayed a reasonably comprehensive line of cabinet-style molded plastic chlorinators in the 1000–2000 lb/day capacity range. Wallace and Tiernan bell jar chlorinators were dedicated to using expensive molded hard rubber parts along with other expensive parts made with silver and tantalum. Their only recourse was to abandon the bell jar line and follow the path of Fischer and Porter, which proved prudent and successful. Some years later one of the key chlorinator design engineers left Fischer and Porter to start his own chlorinator company, which is now known as Capital Controls. It is estimated that these three companies share 97 percent of the chlorinator business in 1983

The most significant advances in equipment have resulted in wider range of chlorine flow control, a greater variety and sophistication of automatic controls and the development of reliable continuous chlorine residual measuring equipment. In 1970, Fischer and Porter developed an analyzer that can measure free chlorine alone in the presence of significant amounts of combined chlorine.[300] Analyzers that measure total chlorine residual have been available since 1950. These have been greatly improved for better reliability.

Advances in safety include remote vacuum chlorine supply systems. This allows the gas from the container to travel to the chlorination equipment under a vacuum, thereby minimizing opportunities for leaks. Development of the remote injector concept has greatly simplified hydraulic problems and piping configurations in chlorinator installations.

Installations are designed to be compatible with strict safety procedures, which include use of container safety kits, leak detectors, and air and nitrogen purge systems of chlorine headers. Safety drills with breathing apparatus and emergency kits are routine exercises at many water departments.

## DEVELOPMENT OF CHLORINATION PRACTICE

### Historical Background

It was found that in addition to destroying disease-producing organisms chlorine can also destroy the nuisance organisms that abound in water supply: those that cause taste and odor, foul the filter media, and degrade the quality of water in the distribution system. Although one of the primary objections to chlorine was that it was enforced medication, a more obvious objection soon rallied many more enemies of chlorination—the chlorinous taste, a byproduct of early disinfection practices. Initially chlorination for disinfection was on the basis of total dosage. Little or no account was taken of water quality or the reactions from the added chlorine. A determination of the effectiveness of the chlorine added was not possible for at least 24 hours, when bacteriologic test results were available.

In 1919, Wolman and Enslow[73] made a most significant contribution to chlorination practice by demonstrating that chlorine absorption could vary widely from water to water. Thus began the first concept of chlorine demand.*

In the same year Alexander Houston reported to the Metropolitan Water Board of London that variable dosages of chlorine will destroy tastes and odors and, moreover, that, the more the chlorine dose is increased, the more certain will be the absence of tastes following dechlorination. These discoveries encouraged an examination of the effects of different chlorine dosages. While there were those who either had no problems resulting from the use of chlorine as a disinfectant or chose to ignore them, there were others who found that they could produce a more palatable water with much higher dosages of chlorine.

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* Chlorine demand is defined as the difference between the amount of the chlorine added to the water and the amount of chlorine (free available or combined available) remaining at the end of a specified contact period.

In 1926 Howard and Thompson[75] reported on an exhaustive study began in 1922 on taste and odor control of the Toronto water supply by means of what they termed *superchlorination* followed by dechlorination. Experiments at Cleveland[75] also tried heavy doses of chlorine to eliminate tastes resulting from industrial waste discharges into the receiving waters of the Cleveland water supply. The most objectionable of these tastes derived from phenols, the same compounds that have plagued most of the water supplies of Europe, particularly those from the Seine and Marne in France and the Rhine and Ruhr in Germany.

Cox[76] reported in 1926 that heavy doses of chlorine could control algae, tastes, and odors in the New York City water supply system. Cox called his method double chlorination, consisting of splitting the chlorine solution discharge from one chlorinator to two points of application instead of one. The heavier dose of chlorine for taste and odor control was ahead of all other treatment. The second point of application was postchlorination for disinfection.

At about the same time Cox and Braidech were experimenting with heavy doses of chlorine, McAmis introduced a new approach to chlorinous taste and odor control: the use of ammonia along with chlorine.[77] The success of the ammonia–chlorine process was so extensive that it practically replaced plain chlorination. This process enjoyed its greatest popularity from about 1930 until 1942. The reason for its decline was twofold: the discovery by Griffin in 1939 of the breakpoint phenomenon, which provided a means for more reliable chlorinous taste and odor control; and the shortage of ammonia nitrogen due to U.S. participation in World War II.

The discovery of the breakpoint phenomenon marked the beginning of the free residual chlorination process. It also sparked a great deal of interest in the kinetics of chlorination and the discovery of the various chlorine residual fractions and analytical methods for their differentiation. It also revived interest in the concept of superchlorination (to a free residual) followed by dechlorination. However, conventional water treatment plants continued to be designed with a variety of locations for the addition of chlorine. In addition to provisions for chlorinating the raw water and the finished water, there was usually a point of application ahead of the filters and another at the entrance to the sedimentation basins. Multiple chlorine application points usually contribute to an overcomplicated chlorine solution piping system, which requires elaborate and expensive flow splitting devices.

## The Chlorination–Dechlorination Concept

**System Description.** When reliable chlorine residual controllers became available in the 1960s, the superchlorination–dechlorination approach was an attractive method for controlling tastes, odors, and sedimentation tank and filter biofouling, as well as providing reliable high-quality water in the distribution system. The term "superchlorination," which was used in the early days, has been replaced by "free residual chlorination."

Using the chlor–dechlor method can achieve the modern approach to the various objectives of chlorination described in the preceding text. The system must be able to apply enough chlorine at the influent of the treatment process to maintain an adequate free chlorine residual into the treated water storage. Then at this point the residual should be controlled automatically by dechlorination.[293] This is in lieu of manually adjusting the prechlorination dosage so that it does not interfere with the postchlorination dosage. Experience has shown that the chlorination process has suffered unnecessarily in a great many instances because the operators were unable, by reason of design, to achieve proper flexibility of application. First, if the plant experiences seasonal problems with tastes and odors, the operator is reluctant to increase the dosage to achieve control of these tastes and odors for fear of having too high a residual entering the distribution system. Second, the operator knows that when he has achieved a substantial free chlorine residual there will be considerable loss from the action of sunlight on the open basins. This causes a wide variation of residual chlorine leaving the plant, which cannot be tolerated. This phenomenon is complicated further by the weather. Changes in the cloud cover introduce another variable, which contributes to additional variation in the residual. Under these conditions it is impossible to calculate hours ahead what the prechlorination dosage must be to achieve the desired residual in the treated water effluent. The chlor–dechlor method eliminates all of these problems.

**The Chlor–Dechlor Facility.** The usual arrangement of this type of system is to use two flow-paced automatic chlorinators for prechlorination. One unit is for standby. One sulfonator is used to apply sulfur dioxide to the finished water. This unit can be operated as a compound-loop system or by direct residual control. The success of the system depends upon the proper maintenance of the chlorine residual analyzer which is used to control the sulfonator. The analyzer can be either the amperometric type or the membrane type. Colorimetric analyzers are not recommended because their response time is much too long.

The arrangement of this equipment to control the residual leaving the plant is simple. Instead of having to bother with postchlorination, the postchlorinator becomes a sulfonator. This unit dechlorinates the treated water to a specified fixed residual. This residual is controlled by the chlorine residual analyzer equipped with a controller. The sulfonator is usually fitted with a flow-paced chlorine metering orifice which receives a flow signal from the plant effluent flow meter. Therefore the sulfonator is arranged to receive two separate signals (flow and residual). This defines the compound loop system. If a flow meter in the treated water line is not available it will be necessary to rely entirely on direct residual control. This method of control has been successful because it has good accuracy over a 7 to 1 range. Never attempt to utilize the plant influent flow meter signal to provide flow pacing for the sulfonator.

The degree of success of this method will depend largely upon the ability to provide the chlorine residual analyzer controller with a well mixed sample. Mixing is described in Chapters 8 and 9

If there is too much loss of free residual in the sedimentation tanks and filters due to sunlight, and if it is not practical or cost-effective to cover these open structures with fiberglass, etc., it may be necessary to superimpose an automatic prechlorination dosage change between day and night operations.

If the primary control is the residual signal, and if the flow of water through the plant does not follow the usual smooth diurnal flow change pattern, as in the case of step rate flow due to pump sequencing, then the chlorine metering orifice should be controlled by an electric step rate controller This step rate flow signal is imperative even if residual control is not involved.

**An Operating Installation.** The following description illustrates the salient features of a chlor–dechlor prototype installation that has been in operation for many years. Fig. 6-4 shows the plant layout and the points of application of chlorine and sulfur dioxide.

The importance of the continuous record of the chlorine residual is illustrated graphically in Figs. 6-5 and 6-6, which show two charts: one from the residual analyzer, and one from a corresponding $SO_2$ flow record of the sulfonator. It can be seen that when the $SO_2$ feed rate has varied from a low of 20 lb/24 hours to a high of 85 lb/24 hours the chlorine residual is practically constant at 0.9 mg/l. Note that at 8:00 A.M. there is an upset in the chlorine residual, due to the backwashing of some filters, with water having zero residual going by the analyzer. At this particular installation the $SO_2$ is mixed in approximately 25 feet of 24-inch line. The steady line on the analyzer chart reveals that it is a good mix. The plant flow rate averages 5 mgd. The prechlorination dosage is changed automatically by a time clock from 6–7 mg/l in the daytime to 3.5–4.5 mg/l at night. This change in prechlorination dosage is to effect an approximate compensation for the free chlorine residual destruction by sunlight. On a bright sunny day (Lat. 35°) the free residual chlorine decay due to sunlight was measured to be as high as 0.5 mg/l per hour.* The residence time in the open basins is long, about 4 hours at average flow. Cloudy days can be distinguished from sunny ones by mere inspection of these charts. The prechlorinator is paced by a flow signal from a metering unit at the influent to the plant. Because there is no metering equipment at the effluent of the plant, the sulfonator is controlled solely by the chlorine residual analyzer

Plants using this system in the western part of the United States use from 2 to 7 mg/l prechlorination dosage to solve seasonal taste and odor problems, and are easily able to have enough free residual at the effluent to be trimmed by $SO_2$ to a final residual of 0.5–0.75 mg/l.

**Controlling THM Formation.** Owing to the success of the chlor–dechlor method it is necessary to consider the problem of THM formation that may result

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* A comprehensive examination of this phenomenon in 1984 at 35° N lat and 5000 ft elev revealed that free chlorine destruction by sunlight on a bright sunny day can be as high as 2.5 mg/l per hour

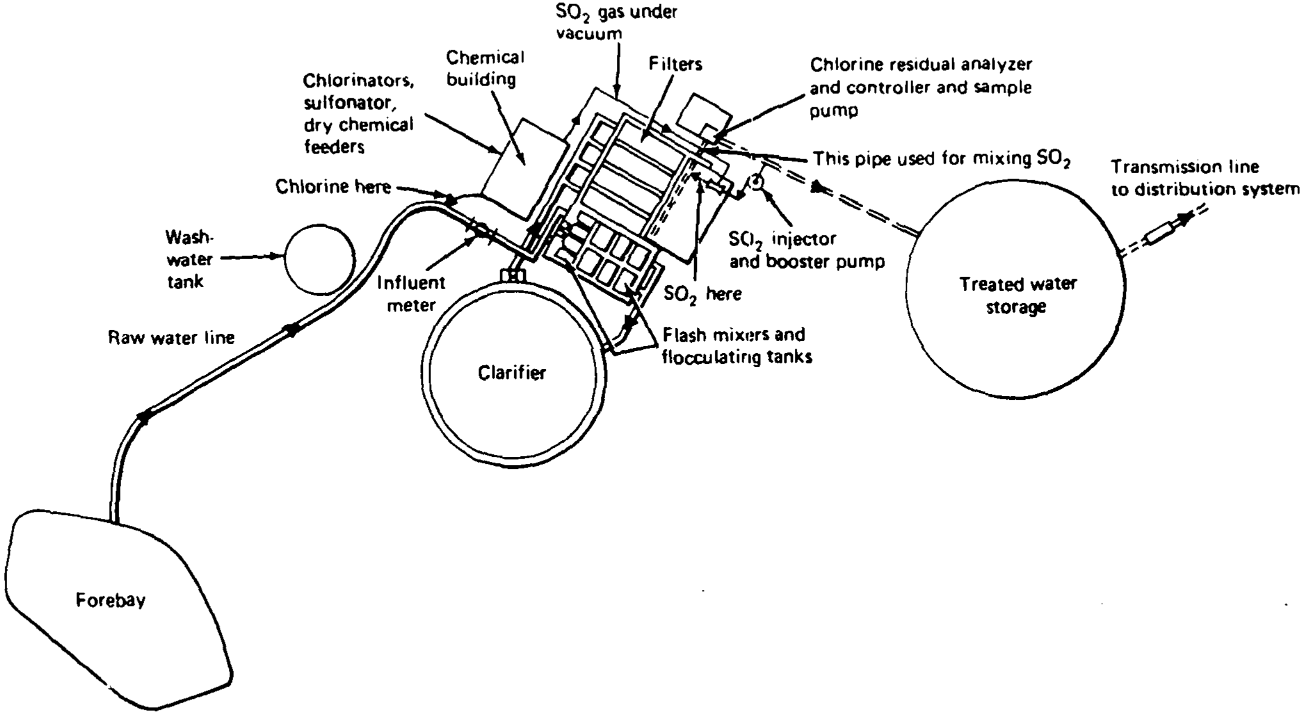

Fig 6-4 The modern approach: Chlorination and dechlorination using residual control. Chlorinators are controlled by electric signal from influent meter plus automatic dosage control. A time clock is used to select two basic prechlorination dosages—one for daytime, and one for nighttime. The sulfonator trims the outgoing residual either up or down in accordance with the set point on the residual analyzer.

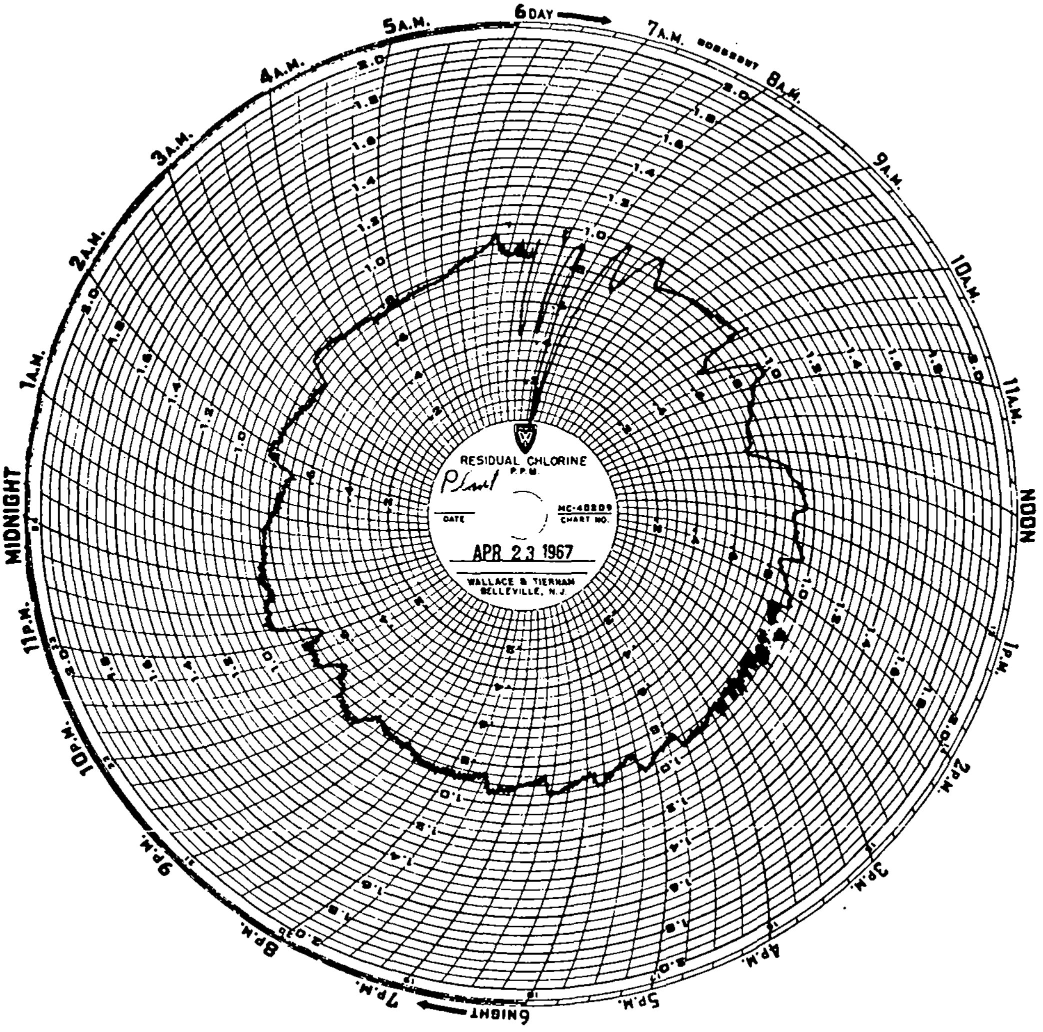

Fig 6-5 A chart from the analyzer showing free chlorine residual.

from a free chlorine residual. To avoid this problem it is only necessary to substitute chlorine dioxide for chlorine in the chlor–dechlor facility, but it remains to be seen whether or not the chlorite and chlorate ions remaining after dechlorination will pose a health hazard. See Chapter 12. The most practical way to control THM (trihalomethane) formation is to use the ammonia–chlorine process. This obviates the use of the free residual process.

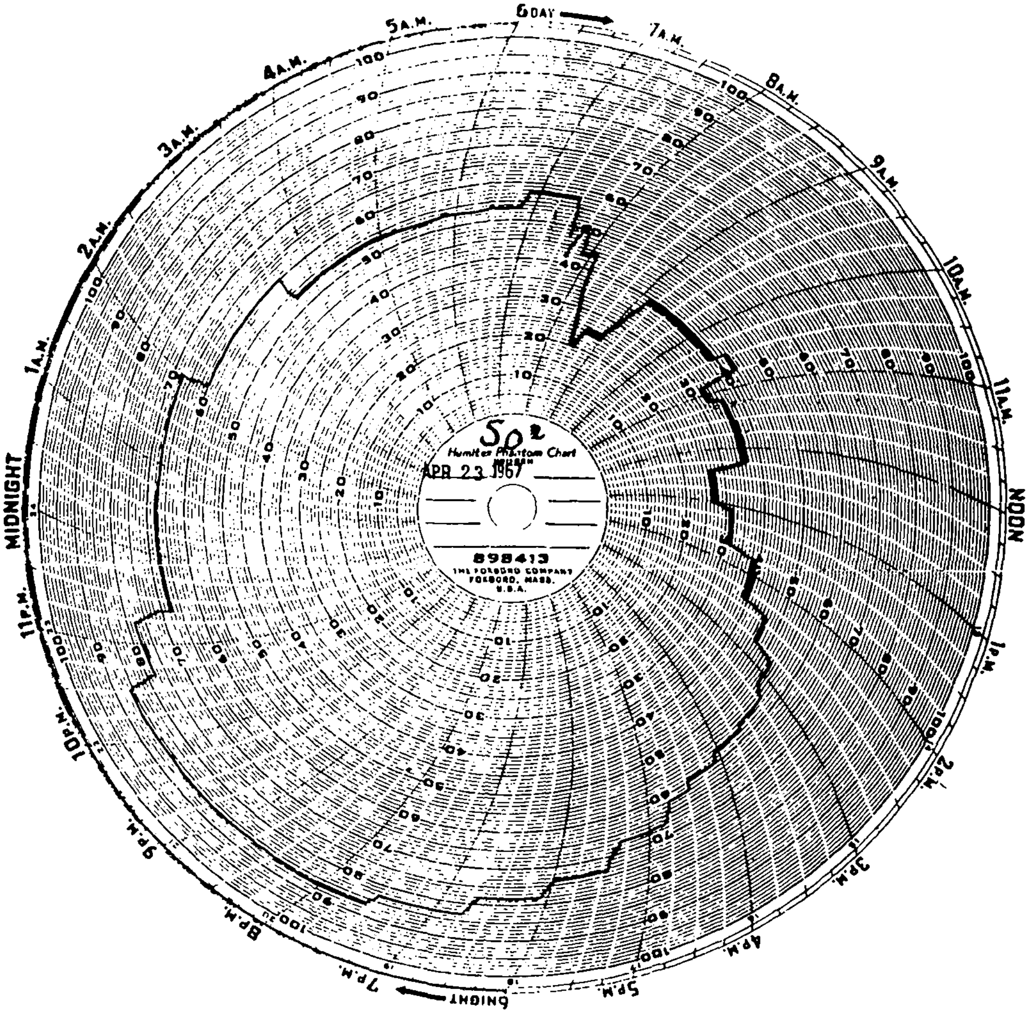

Fig 6-6 Chart from the sulfonator showing record of $SO_2$ feed rate corresponding in time to analyzer chart. Reprinted from *Journal American Water Works Association* **60** (5) May 1968, by permission of the Association.

**Complete Dechlorination Followed by Rechlorination.** There are many waters that could benefit from this technique, in particular those that develop taste and odor problems caused by objectionable concentrations of the nuisance residuals beyond the breakpoint. In this procedure dechlorination does not remove the ammonia-N bound up in these residuals. It remains to form true monochloramine in the rechlorination step. The objectionable nuisance residuals are removed, which is the great advantage of this procedure. Since rechlorination is designed to be in the range of 3–5 to 1 chlorine to the remaining ammonia nitrogen there is no danger of any nuisance residuals forming. The end result is in fact the ammonia–chlorine process preceded by the free residual process.

This is an extension of common practice in many plants which follow the rule: free chlorine through the plant and chloramine in the distribution system. There are of course exceptions, particularly in view of the necessity to avoid excessive THM formation. There are some waters that cannot be cleaned up with free residual chlorination.

## The Ammonia–Chlorine Process

**Historical Background.** The use of ammonia with chlorine in water treatment has an unusual history. Both its discovery and use were largely by accident. Fritz Raschig[80] in 1907, while working with aniline and hypochlorite, noticed that no color developed when these two compounds were reacted in the presence of ammonia. This aroused his wish to experiment further with these compounds. By reacting two parts by weight of chlorine and one part of ammonia, he was able to produce a compound resembling a faint yellow oil. He termed this compound chloramine in accordance with the following equation:

$$NaOCl + NH_3 \longrightarrow NH_2Cl + NaOH \qquad (6\text{-}1)$$

Raschig's experimental work provided the theoretical basis for the later application of chlorine and ammonia in the water treatment field. Race[81,83] was probably the first to use the ammonia-chlorine process. He was in search of a method that would reduce the cost of chlorination, and was influenced by some observations by Rideal,[294] who noted that during the chlorination of sewage bactericidal action continued even after all the hypochlorite had "disappeared." Rideal attributed this continuing action to the influence of ammonia in the sewage. After performing successful laboratory experiments with ammonium hypochlorite, Race adopted this method in 1916 at the principal treatment plant at Ottawa, Ontario. Purely by an accidental error of some sort, his findings indicated that ammonium hypochlorite had three times the germicidal action that bleaching powder (calcium hypochlorite) did. Plant scale operations convinced Race that it was a more economical method than chlorine alone and, furthermore, that the finished water was free from objectionable tastes and odors, which he attributed primarily to the decrease in dosage.

In view of present-day knowledge, both of his conclusions were incorrect. Race also noted the elimination of aftergrowths following the prolonged use of ammonium hypochlorite. The first installation in the United States was made at Denver in 1917.[295] Alexander Houston[24] paved the way, in the development of preammoniation, to prevent taste formation caused by the reactions of chlorine and organic matter.

Although the first successful application of the ammonia-chlorine process for taste and odor control in the United States was by McAmis[77] in 1926, it was not until the work by Harold[86] and Adams[87] in England, and by Lawrence[88] and Braidech[89,90] at Cleveland, Ohio, that the possibilities of the process were fully realized. After the intensive investigation (five months and nine thousand tests) of Lawrence and Braidech, this process for taste and odor control achieved nationwide prominence. This was due in part to a previous investigation by Ellms and Lawrence[91] in 1921 on the same water, in which they submitted that waters polluted by phenols did not respond to superchlorination followed by dechlorination with activated carbon.

The Cleveland investigation concluded that preammoniation prevents tastes and odors with phenol concentrations as high as 1.0 mg/l, and that combined residuals up to at least 0.6 mg/l can be maintained without producing chlorinous taste and odors. This was considered a high chlorine residual because at this time an acid O-T residual of 0.2 to 0.3 mg/l was considered adequate.

The installations at Cleveland began in November, 1929, at the Division plant, followed two months later at the Baldwin Street plant. Other successful installations were reported at Springfield, Illinois, by Spaulding in 1929,[92] at Lansing, Michigan, in 1929 by Harrison,[93] and at Lancaster, Pennsylvania, by Ruth in 1931.[94] These successes created a great demand for the process, which resulted in some miserable failures because of ignorance of the limitations of the process.

This process enjoyed its greatest popularity between 1929 and 1939. Two years after the Cleveland installations, there were 190 other installations. In 1938, based on replies to a questionnaire from 2541 supplies in thirty-six states, 407 of these supplies used ammonia with chlorine.[98] In 1958 Griffin and committee sent out a questionnaire to 114 municipalities. Among the eighty-five answers, only seven reported preammonia; twenty-six reported postammonia; two, both pre- and postammonia. The surprising number of users of postammoniation was probably for treatment of high *p*H waters. The process fell into a rapid decline shortly after the discovery of the breakpoint phenomenon in 1939. This, coupled with the inability to purchase ammonia during the war years (1941–45), relegated its use to cases of special treatment.

**General Discussion.** This process involves the addition of ammonia and chlorine compounds separately to a water processing system. These compounds are usually anhydrous ammonia and hypochlorous acid. The combination forms chloramines. This procedure can also be called chloramination or the chloramine process. In general, when the ammonia is applied first it tends to prevent the formation of compounds that would otherwise produce chlorinous taste and odors. However, there are many instances where ammonia is added to a water containing a combination of free and combined residual for the sole purpose of converting all the free residual to combined residual. This has been well documented by Williams.[78,79] This technique of free residual conversion to chloramines has been called dechlorination by ammonia. This is a misnomer, because it does not remove any chlorine compounds. One disadvantage of this procedure is the inability of the ammonia addition to remove any of the nuisance residuals that may have formed in the free residual process. However, it is common practice to add ammonia to a water containing free residual to purposely provide chloramine residual in the distribution system.

Conversion of free residual chlorine to chloramines is standard practice in high pH waters, including waters that are softened by the excess lime process.

The preferred ratio of chlorine to ammonia-N has been documented as 3:1. This ratio appears to produce the best tasting water. The ratio for maximum disinfection efficiency is 6:1; therefore, each application should be ratio tested in the laboratory to find acceptable taste close to maximum disinfection efficiency.

There has been a great surge in the interest in the ammonia–chlorine process since 1979. This is the result of the discovery that chloramines do not form THMs.

Before the discovery of the breakpoint phenomenon this process was used primarily for the control or prevention of chlorinous tastes and odors in the finished waters. Its widest use has been in the maintenance of chlorine residuals in a distribution system. It is almost universally successful in preventing the degradation of water quality that might otherwise result in tastes and odors and discolored water from bacterial action. Its success is due to the fact that a chloramine residual can persist many times longer than a free chlorine residual, and therefore is able to penetrate into stagnant areas of a system. It is also very useful for the same purpose on long transmission lines, where it is necessary to preserve carrying capacity.

The application of ammonia with chlorine should be evaluated on the merits of each individual case. In some instances it has been known to successfully prevent the formation of chlorinous tastes by being used to *induce a breakpoint.** In another instance ammonia was applied to three separate raw water sources from the same watershed at the rate of 1 lb/mg, followed ten minutes later by 19 to 20 lb/mg chlorine. This produced a water free of taste and odor with a free chlorine residual between 1 and 2 ppm. When chlorine was used alone on this water, a chlorophenol-like taste developed that did not respond to super doses of chlorine, but persisted for months. The source of the phenol-like compounds contributing to these chlorinous tastes was unknown.† Therefore each water that develops obnoxious tastes and odors resulting from chlorination may benefit by the use of the ammonia–chlorine process for the prevention of such tastes. This procedure began 35 years ago and is still being used today (1983).

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* This procedure, used by O'Connell and Harvill,[95,97] proved successful in the Houston water supply problems in the 1940s.

† The source of these compounds was found to be from the Quaking Aspen tree (Poplar trimulus) on the watershed.

After the discovery of the breakpoint phenomenon in 1939, the ammonia–chlorine process fell into a sharp decline because the free chlorine residual produced by the breakpoint procedure proved to be equally effective in either controlling or eliminating taste and odors. Other additional benefits that were not necessarily common to chloramine residuals were also discovered. The demise of the ammonia-chlorine process was nearly complete during World War II. It was almost impossible to get any ammonia nitrogen compounds during the war (1941–1945). But its use did continue on a limited basis during these times because there was still a sizeable segment of the practitioners in water quality control who believed in chloramine residuals to maintain water quality in the distribution system. This and other practices using chloramines continue today (1983).

**Germicidal Efficiency.** The fate of this process was in some doubt when the EPA labeled chloramines a secondary disinfectant in 1978.[99] The EPA outlined certain conditions that would allow the process to be used. The most acceptable situation was to apply the chlorine first, then apply the ammonia after 10 minutes contact time with chlorine alone. As of 1983 the ammonia–chlorine process is now accepted by the EPA as a primary disinfectant provided contact time is adequate and that there is proof of disinfection. This is largely due to the fact that the addition of ammonia before chlorine prevents the formation of trihalomethanes. There are some waters that cannot comply with EPA MCL limitations of THMs when the chlorine is applied before the ammonia; therefore these waters must rely on the ammonia–chlorine process to meet EPA standards.

The EPA originally labeled chloramines as secondary disinfectants because of extensive evidence that free chlorine residuals are 100 times more germicidal than chloramines. This conclusion was based upon studies involving short contact times, 5 minutes or less, and some of the methodology and residual detection methods used are suspect. But in 1967 Morris derived a lethality coefficient which showed that HOCl is 200 times more lethal to enteric bacteria at 5°C than is monochloramine after 10 minutes contact time.[100] This is why the EPA allowed the use of chloramines as a primary disinfectant provided there was a full chlorine residual for ten minutes prior to the addition of ammonia.

**Treatment Plant Research.** Recent research in the use of chloramines for water reuse situations reveals an entirely different concept of the germicidal efficiency of chloramines. The plant scale investigations by the Sanitation Districts of Los Angeles County[101] developed criteria for disinfection of wastewater to be used for bathing and reuse. Their work revealed that chloramines were almost as good as free chlorine both as a bactericide and as a virucide. This efficiency is based upon good mixing and contact times of 50–60 minutes with the same chlorine dose.

Of equivalent significance is a study by Selleck et al.[102] at the University of California Sanitary Engineering Research Laboratory, Richmond, California. This study revealed that the germicidal efficiency of chloramines is practically equal to that of free chlorine provided the contact time is long enough and provided the ratio of chlorine to ammonia is such that the residual falls on the slope of the curve between the hump and the breakpoint.

The Metropolitan Water District of Southern California has made a lengthy pilot plant study to evaluate THM formation and disinfection efficiency of chloramine using a chlorine to ammonia ratio of 3 to 1 by weight.[103] Taste and odor formation and other chlorine to ammonia ratios were not investigated. They studied three schemes of ammonia–chlorine application in addition to free chlorine. These schemes were:

1. Sequential chloramination: chlorine upstream from the rapid mixer, then ammonia 17 minutes later downstream from flocculation and upstream from sedimentation
2. Concurrent chloramination: chlorine upstream from rapid mixer, then ammonia 50 seconds later in the rapid mix basin
3. Preammoniation: ammonia added in the rapid mix basin followed by chlorine in the flocculation basin

The lowest levels of THM formation were observed for the concurrent and preammoniation schemes.

The point of application of chlorine and ammonia did not affect the occurrence of coliform bacteria in the pilot plant effluent. They were uniformly absent. This finding agrees with others: given long contact times free chlorine and chloramine residuals are equivalent disinfectants (based upon coliform kill).[101,102,170-172] The contact time from influent to effluent in the pilot plant was 3 hours 21 minutes. However, coliforms were observed on 13 occasions upstream from the sedimentation basins (17 minutes contact time) using the preammoniation scheme.

The use of the Millipore standard plate count procedure (m-SPC) bacteria indicated that preammoniation produced higher pilot plant effluent total plate counts than concurrent or sequential addition of ammonia or free chlorine. This disparity between the total plate counts of the different chloramination schemes was thought to be the result of preammoniation interference with the physical removal of particulate material (including bacteria). However, no statistical difference in effluent turbidity was found for the ammoniation schemes. Therefore the higher plate counts appear to be due to the reduced bactericidal efficiency and not compromised filtration efficiency.

**Factors Affecting the Efficiency of the Process.** The preferred sequence of chemical addition is usually ammonia first and then the chlorine. The ammonia must be well dispersed before the chlorine is added. This is a critical factor. When the chlorine is added it must be mixed as quickly as possible (2 sec). This is necessary because the reaction between ammonia and chlorine solution at the *p*H range of 7–8.5 is practically instantaneous. If mixing is slow or poor, side reactions between the chlorine and organic matter can interfere with the formation of true chloramines. An example would be organic matter subject or prone to bleaching by chlorine solution.

White et al.[172] found that in a high-quality tertiary effluent, mixing at the point of application greatly affected the bactericidal efficiency of the chloramine process. In this particular case the ammonia was added to a completely nitrified and filtered effluent which passed through a pumping cycle before the chlorine was added. The chlorine solution was mixed with turbine-type mechanical mixers. The total coliform count with the mixers was usually about 13–20/100 ml MPN. With no mixing the count was 1300/100 ml MPN or greater.

Water temperature affects the reaction time between ammonia and chlorine. The reaction is significantly retarded at temperatures below 50°F. Treatment plant operators in cold areas should be cognizant of this because it can effect the location of the point of application of each chemical.

**Pretreatment Problems.** When using the ammonia–chlorine process as a pretreatment process in which rapid sand filters are involved, certain precautions must be taken. An addition of ammonia in excess of chlorine can promote the growth of nitrifying bacteria in the filter beds. Since chloramines will not react to destroy nitrites, and since the excess of ammonia acts as a nutrient, the nitrifying bacteria will proliferate. Then it becomes necessary to destroy the bacteria and the nitrites by free chlorine. If a proper ratio of chlorine to ammonia is maintained, including the natural ammonia content of the water, and if an adequate chloramine residual (0.5–1.0 ppm) is maintained at the discharge of the filters, such difficulties with nitrifying bacteria will not occur. To eliminate all possibility, the operator should not use the acid O-T method for residual determination when using a combination of chlorine and ammonia, because if nitrites do develop, they cause a significant false O-T reading. Use instead the amperometric titration procedure or the DPD–ferrous titrimetric method.

### Disadvantages of the Ammonia–Chlorine Process

**Effect upon Water Quality in Distribution Systems.** A significant disadvantage of the chloramine process is that the addition of ammonia to a water does provide nutrients sufficient to cause algal blooms in reservoirs and an increase in distribution system bacteria population, which might not occur otherwise. This situation can be avoided by the continual presence of a chlorine residual regardless of contact time.

Fortunately, contact time has no effect upon THM formation by chloramines. Therefore the nutrient factor can be overcome by maintaining a residual regardless of the length of contact time. If the system is too spread out to maintain a residual, then rechlorination may be necessary. In this instance only chlorine is required.

When the residual disappears the chloramines revert to ammonia in the form of $NH_4OH$.

**Effect upon Kidney Dialysis Patients.** Kjellstrand et al.[300] reported that chloramine residuals in tap water pass through reverse osmosis membranes in dialysis machines quite easily. Furthermore, they directly induce oxidant damage to red blood cells, resulting in methemoglobin formation and damage to the HMPS with which red cells defend themselves against oxidant damage, which induces hemolysis and short red cell survival time. Moreover, they sensitize the patients to oxidant drugs like primaquine, sulfonamides, etc.

The effect upon the patient is apparently directly from the chloramines and not from any nitrogen compound associated with the chloramines. When Kjellstrand experimented with ascorbic acid as a dechlorinating agent there was no detectable methemoglobin formation. Ascorbic acid reduces chloramines* to hydrochloric acid and ammonia.[300]

*Activated carbon* has been thoroughly investigated as an acceptable method for the dechlorination of both free chlorine (HOCl) and chloramines ($NHCl_2$, $NH_2Cl$, and $NCl_3$).[302-304] The most difficult species to dechlorinate on a predictable basis are the chloramines. Meyer and Klein[301] investigated the use of granular activated carbon (GAC) as a practical method to remove chloramines from dialysis water. They found that the dechlorination capacity of three different carbons differed as much as one order of magnitude. They further estimated that a 1.5 mg/l chloramine residual could be reliably removed during 156 5-hour dialyses with a GAC column.

*Ascorbic acid* is a more positive method and is appealing because of its simplicity. There is no danger of any chloramine breakthrough into the dechlorinated water provided the ascorbic acid dosage is adequate and the application is reliable. The GAC method requires careful monitoring to avoid chloramine breakthrough as the carbon approaches exhaustion.

Experience has shown that the use of GAC for dechlorinating chloramines is site-specific. Therefore any water containing chloramines to be dechlorinated should be bench tested to determine precisely the equipment required for a particular carbon source to be used.

**Effect upon the Aquarium.** Chloramines represent a two-pronged toxicity dilemma to aquatic life. Both chloramine residuals and unionized ammonia are toxic to fish in very low concentrations. The mechanism of chloramine toxicity is as follows: Chloramines pass readily through the permeable gill epithelium with an insignificant amount of cell damage. Once the chloramines have entered the bloodstream they chemically bind to iron in hemoglobin in red blood cells. This cripples the ability of the cells to bind oxygen. This condition is known as methemoglobinemia. It is similar to the oxidation of hemoglobin caused by nitrite toxicity.[305,306]

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* The types of chloramines were not identified

When monochloramine is dechlorinated by a reducing compound which produces sulfurous acid ($H_2SO_3$), ammonium chloride is formed as follows:

$$NH_2Cl + H_2SO_3 \longrightarrow NH_4Cl + H_2SO_4 \qquad (6\text{-}2a)$$

Ammonium chloride ionizes to form ionized $NH_4^+$ and unionized $NH_3$ nitrogen (ammonia). Therefore all of the ammonia utilized to produce monochloramine is returned to the water as shown in Eq. (6-2a), $NH_4^+ + Cl^-$. This represents total ammonia. To avoid fish toxicity unionized ammonia must be limited to 0.025 mg/l. Unionized ammonia concentration can be calculated from total ammonia. See Chapter 7. The maximum allowable total ammonia is about 0.4 mg/l at *p*H 8.3 and 70°F in a marine aquarium.

Therefore ammonia removal is also a must for the aquarium when chloramines are dechlorinated chemically. In aquatic systems such as an aquarium, ammonia accumulates from nitrogenous wastes released directly from the fish and from deamination of protein in food and wastes by heterotrophic bacteria. However, nature provides a mechanism that serves to control ammonia buildup. It is called nitrification. It is the primary means of ammonia removal in fish culture systems.[307] By this process, ammonia is oxidized to nitrate in two separate steps, each step dependent upon and controlled by a specific group of bacteria:

$$NH_4^+ + \frac{3}{2}O_2 + \textit{Nitrosomonas}\ \text{Group} \longrightarrow NO_2^- + 2H^+ + H_2O \qquad (6\text{-}2b)$$

$$NO_2^- + \frac{1}{2}O_2 + \textit{Nitrobacter}\ \text{Group} \longrightarrow NO_3^- \qquad (6\text{-}2c)$$

Simply placing fish into an aquarium with a recirculation filter will initiate the growth of these two groups of bacteria because they exist naturally in the environment. Unfortunately, these bacteria grow slowly, so they need a conditioning period to attain the necessary population to limit the production of the ammonia produced by the aquatic culture.

Removal of the ammonium ion ($NH_4^+$) is best accomplished by naturally occurring zeolites known also as clinoptilolites. Zeolites have a high selectivity for $NH_4^+$ removal, which decreases the toxic unionized ammonia concentration. They are relatively inexpensive and commercially available. They have been used for many years in industry as a freshwater demineralizer.[305,307]

Finally it should be pointed out that the toxicity of ammonia decreases with *p*H. If the *p*H of the system is below 7 the ammonia produced will not be a problem in the aquarium. For example: in water at *p*H 6.9 and 75°F, 99.58 percent of the ammonia will be in the nontoxic ionic form. However, at the same temperature, but at a *p*H of 8, ammonia will be 9.49 percent ionic.[305]

*Activated carbon* has been used with moderate success to dechlorinate chloramines in potable water treatment processes, but its principle role is to adsorb organics in order to eliminate taste and odors. It is a popular filter material used in the aquarium industry for the filtration of fresh water and marine aquaria. It is a porous material that removes molecules from solution by binding them to the carbon's surfaces by a process known as *adsorption*. When carbon removes chloramines, ammonia is formed in the early stages of the adsorption process, followed by a decrease in ammonia as it is converted to nitrogen gas. This reaction occurs with predictable results if the carbon has been seasoned by exposure to residual chlorine. When chloramines come in contact with virgin carbon the chloramines are destroyed, but some of them revert to ammonia as the surface of the carbon oxidizes and chloride ions are released into solution.[305] If the carbon has been previously exposed to chlorine the carbon surface is coated with oxides which prevent the formation of ammonia by chloramine reversion. Therefore the surface reaction of the chloramines and carbon results in a combination of adsorption and catalytic oxidation, releasing nitrogen gas and chloride ions and lowering the water *p*H.

**General Summary.** For dialysis systems ascorbic acid for dechlorination seems to have all the practical and reliability assets. Activated carbon and some green sand zeolite are also capable of achieving complete dechlorination.

Aquaria require much more treatment because both chlorine residuals and ammonia are toxic to aquatic life. Dechlorination plus ammonia removal can be accomplished in one step using activated carbon provided the system is carefully planned and properly designed. Dechlorination can be easily accomplished by chemicals such as the sulfite ion species or thiosulfate. The latter is not recommended, however, because it is too expensive and has a longer stepwise reaction. Following chemical dechlorination the ammonia can be removed by the use of zeolites. The zeolite removal process is similar to a water softening system.

**American vs. European Practice: A Paradox.** The paradox is the current European limitation on the allowable ammonia nitrogen concentration in the finished water (0.05 mg/l) vs. the allowable addition of ammonia nitrogen to U.S. drinking water to form chloramines which prevents the formation of THMs.

*European Practice.* The ammonia–chlorine process was never practiced as such in European treatment schemes because most of the surface waters contained an abundance of ammonia nitrogen. The source of ammonia nitrogen derived mainly from untreated sewage and industrial wastes. Therefore the European treatment schemes used prechlorination for nitrogen removal. This in turn allowed the practice of free residual chlorination. In some instances as much as 20 mg/l chlorine were required to achieve the breakpoint.

The detection of trihalomethanes where free residual chlorination of polluted waters was practiced and the general undesirability of ammonia nitrogen in potable water resulted in some significant changes in European water treatment practices. There is no question that ammonia interferes considerably with the disinfection process, particularly when that process is free residual chlorination. This circumstance, coupled with the observations that trihalomethane concentrations increase as free chlorine residuals increase, was considered by the European community of water producers as grounds for elimination of ammonia nitrogen in potable water supplies. Although it is never mentioned as such, one of the dominating factors against ammonia nitrogen, particularly in U.S. supplies, is the nutrient factor, which eventually contributes to water quality degradation in reservoir systems, long transmission lines, and widespread distribution systems unless adequate chlorine residuals can be maintained.

European water purveyors were thus made subject to an agreement by the ministers of the European Economic Community on December 19, 1978, limiting the allowable ammonia-nitrogen concentration in water delivered to the consumer to 0.05 mg/l. Moreover, the ministers decreed that the method of nitrogen removal to comply with the limitation must be biological nitrification. Realizing that such a drastic change in the treatment procedures would take time, the use of chlorine for nitrogen removal was allowed until installation of the recommended system was found practicable.

As of 1979 the agreed upon treatment train for nitrogen removal where applicable and possible included: raw water ozonation at a fixed dosage; groundwater storage followed by coagulation, sedimentation, and filtration followed by ozonation; and then biological nitrification followed by chlorine dioxide for effluent disinfection.

Actually, effluent disinfection by either chlorine or chlorine dioxide was required, for ozone was not generally accepted as the final disinfectant. Intermediate points of chlorination or chlorine dioxide are acceptable provided they do not interfere with biological nitrification. This is a two-step process of ammonia oxidation which involves the formation of nitrites. The conversion of nitrites to nitrates is the final step in ammonia removal. This is accomplished by the *Nitrobacter* species of bacteria. Oxidation of nitrites and/or destruction of the *Nitrobacter* bacteria by chlorine or chlorine dioxide may either interrupt or destroy the nitrification process. Therefore the addition of either chlorine or chlorine dioxide at intermediate points must be carefully selected.

Rittman and Snoeyink[309] (1984) presented a comprehensive review of European practice together with the microbiological theory demonstrating how biological processes within a water treatment plant can remove the organic and inorganic substrates that promote biological instability, the root cause of biofouling in a distribution system. A biologically stable water is one which does not support the growth of microorganisms to a significant extent, whereas an unstable water results in high numbers of microbes in the distribution system unless persisting chlorine residuals are maintained.

Rittman and Snoeyink[309] investigated both French and British practices of nitrification using biological filters, fluidized bed filters (also called biological sedimentation filters), rapid sand filters, and granular activated carbon beds. All of these processes are biofilm reactors that achieve nearly 100 percent ammonia removal even at low temperatures.

While the primary objective of these processes is to remove ammonia nitrogen they simultaneously remove a significant proportion of the natural chlorine demand of the raw water. This allows the Europeans to disinfect at lower chlorine dosages, which eliminates, in their view, the THM hazard. If chlorine dioxide is used its demand is likewise lowered, thereby eliminating fears of high concentrations of chlorate and chlorite ions.

*United States Practice.* In 1980 the EPA changed its stance on the use of chloramines as a disinfectant for potable water. It was allowed to become a primary instead of a secondary disinfectant. This provided an easy solution to those water producers who were plagued with unacceptable THM levels caused by free chlorine residuals. Understandably this revived the ammonia–chlorine process in the U.S.A.—so much so that in the long run it may do more harm than good. A 1984 report of a 50-state survey by Hack[310] revealed that 53 percent of chloramine users claimed distribution system residuals in the 3–4 mg/l range. Such residuals would be appalling to Europeans. This practice of high residuals to maintain water quality will eventually lead to greater problems.

It is unfortunate that chloramines do not contribute to the formation of THMs. Otherwise water producers in the U.S.A. would have to clean up the raw water, thereby reducing the chlorine demand. This would allow significantly lower doses of chlorine and/or chlorine dioxide and would provide biologically stable water to enter the distribution system.

What the water industry needs now is to put a ceiling on chlorine dosages. White has been advocating for years that an arbitrary limit of about 2.0 mg/l be placed on the 15-min chlorine demand for any raw water supply. When compared to European practice this may be too high. To put chlorine demand in perspective one only has to look at the 15-min chlorine demand of this planet's natural water source—seawater. It rarely exceeds 1.5 mg/l. A limitation on *chlorine demand* should be a surrogate parameter for raw water quality. If the limit is exceeded then the water would have to undergo special pretreatment to reduce the 15-min chlorine demand to the acceptable level.

**Blending Chloraminated Water with Chlorinated Water.** The Metropolitan Water District of Southern California changed its primary disinfectant from free chlorine to chloramine in 1984 to help its member agencies control THM formation. Problems of taste and odor complaints were anticipated so they designed a laboratory study to determine the effects of blending chloramine residuals with chlorine residuals by developing blend-residual curves to simulate the systems involved.[311] The potential problems of blending are related to a mixture that proceeds through the breakpoint curve which allows the formation of dichloramine and possibly nitrogen trichloride. These two compounds are notorious for causing consumer complaints. MWD decided on a 3:1 Cl–N ratio for chloramination. Using this ratio and accounting for the almost negligible concentration of naturally occurring ammonia-N they developed an induced breakpoint curve for each of their two supplies: (a) The Northern California water supply known as state project water (SPW) and (b) the Colorado River water labeled CRW. The induced breakpoint of the SPW at *p*H 7.5 occurred at a Cl–N ratio of 11:1 and for the CRW at *p*H 7.9 the ratio was 9.2:1. These breakpoints occurred after 4 hours in the dark at 25°C. They followed this with a series of breakpoint curves due to blending. Two of these are shown in Figs. 6-6a and 6-6b, which illustrates the same two waters at contact times of 5 minutes and 4 hours. These figures demonstrate that at short contact times all of the chlorine species may exist together in the breakpoint region.

From this experimental work the MWD staff developed a computational model that allows the prediction of acceptable blends of chloraminated and chlorinated waters without experimentally determining each case. They anticipate the need of further analyses as a check on the distribution system to see if there may be occurrences of Cl–N ratios greater than 5:1. If such a situation exists it becomes bacteriologically significant at ratios of about 6.5:1. From this point forward the chlorine residual decreases rapidly to nearly zero at the breakpoint where disinfection ceases entirely. This is a more serious situation than a consumer taste and odor complaint.

## Advances in Chlorination

Attempts to explain Griffin's findings[104,105] led to serious scientific investigations during 1946–1950. The work of Fair, Morris, Chang, Weil, Burden, and Culver[106-108] is largely responsible for our present knowledge of the kinetics of chlorination.

In 1950 Palin[109,110] in England did some masterful work on the kinetics of the breakpoint reaction and the distribution of various chlorine residual fractions. In 1954 Granstrom[111] explained the breakpoint phenomenon. Then Williams of Canada, working with a most difficult water, proceeded to substantiate the laboratory findings of both Palin and the Harvard group.[112-114]

In the pursuit of his research work on chlorination, Palin directed his attention toward the analytical measurement of chlorine residuals. He wanted to be able to quantify each chlorine residual fraction such as free chlorine, monochloramine, dichloramine, and nitrogen trichloride. His many years of work resulted in the DPD method of residual differentiation.[115,116] In addition to the chlorine fractions, Palin developed procedures for chlorine dioxide, chlorite ion, bromine and ozone.[117] The titrimetric procedure using ferrous ammonium sulfate as the titrant is a favorite with researchers.

However, the amperometric titrator remains the most popular method among

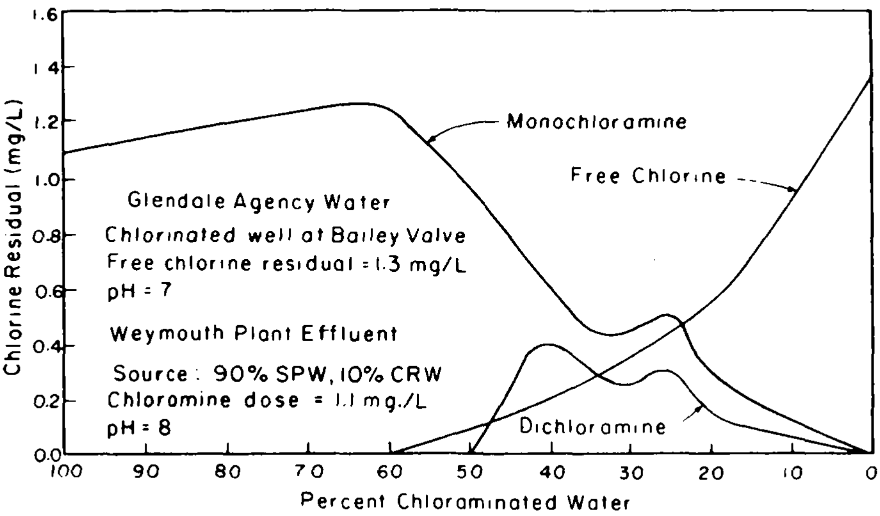


Fig 6-6a Chlorine residual curves for Glendale California chlorinated well water blended with Weymouth treatment plant chloraminated effluent after 5-min contact time.[311] (courtesy Metropolitan Water District of Southern California).

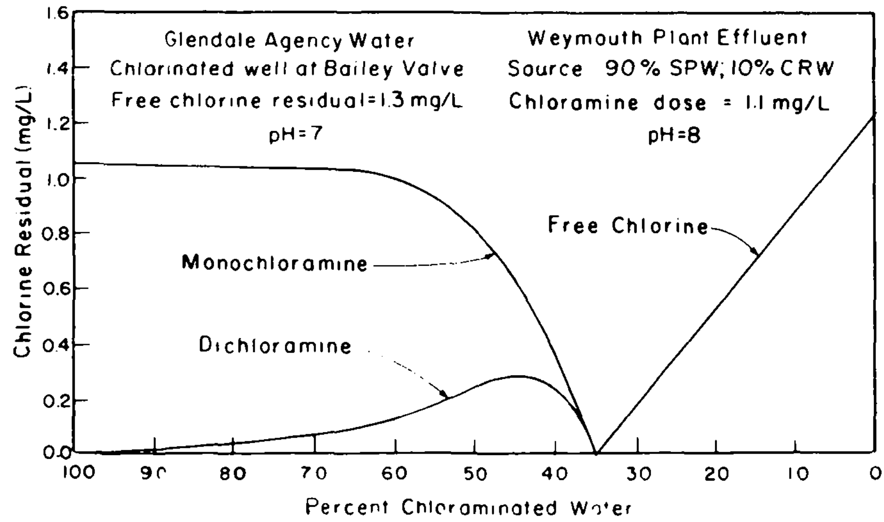


Fig 6-6b Chlorine residual curves for Glendale California chlorinated well water blended with Weymouth treatment plant chloraminated effluent after 4-hour contact time.[311] (courtesy Metropolitan Water District of Southern California).

operators who need to differentiate between free and combined chlorine. As the titrator is portable it is well suited to field work for on-sitė determination of chlorine residuals. It is also the most popular method in wastewater and water reuse situations. Orthotolodine is still being used but is rapidly being replaced by the colorimetric DPD tablet method and the FACTS method. Orthotolidine lost its popularity when it was discovered that the orthotolidine powder was a carcinogen that affected the urinary tract of workers who prepared the indicator solution.

The most recent laboratory research on the dynamics of chlorination and the breakpoint phenomenon was by Wei and Morris[118] in 1972 at Harvard and by Saunier and Selleck[119] at the University of California, Berkeley in 1976. This work explained in much greater detail the kinetics of chlorination and provided a more precise explanation of what actually does trigger the breakpoint. Moreover computer models were developed which provide the practitioners with a tool for predicting what will occur in a given situation.

Although the laboratory research work taught the industry about the theoretical aspects of chlorine and ammonia reactions, it was the work by Williams[120] on a plant scale basis which showed the practical effects of chlorinating a water containing both ammonia nitrogen and organic nitrogen. His work demonstrated that chlorination in the presence of organic nitrogen formed an unusually stable chloramine compound which differentiates as the dichloramine fraction in either the amperometric or DPD–FAS procedures. This has since been confirmed by many others.

Some of the most important advances in chlorination have been the improvement in the metering and control equipment. Automatic residual control was not available in North America until about 1960. Before that time Wallace and Tiernan had made some custom-designed residual controllers (using orthotolidine color as the control) for special situations. About 1950 Wallace and Tiernan of Great Britain began offering automatic residual control. Even though Wallace and Tiernan U.S.A. had already developed the amperometric titrator and the amperometric residual recorder by 1950, it was another decade before they believed that their new line of chlorination equipment was capable of combining flow pacing with residual control. Since 1960 a wide variety of control modes have been available from both Wallace and Tiernan and Fischer and Porter. Since about 1976 Capital Controls has been offering flow pacing combined with residual control. These developments have increased the reliability of the chlorination process.

## The Free Residual Process

**Role of Ammonia Nitrogen.** This process is the implementation of the breakpoint phenomenon The chemistry of this phenomenon is described in Chapter 4.

Free residual chlorination as a process was a direct result of the search for a better way to produce a palatable water than by the ammonia–chlorine process.

This search was accomplished in the field and laboratory almost simultaneously on opposite ends of the U.S.A by Griffin[121,122] and O'Connell[123] in 1939. After literally thousands of tests on different waters, with different dosages and contact times it was found that the optimum residual for the most palatable water should contain 85 percent free chlorine.

This process is based upon the fact that a free residual ($<5$ mg/l HOCl) does not impart any off-flavor to the water. Moreover this species of chlorine residual fraction is by coincidence the most germicidal.

In the free residual process, sufficient chlorine is added to destroy the ammonia nitrogen. This occurs when the ratio of chlorine to ammonia nitrogen (as N) is about 10:1 by weight. However, the stoichiometric ratio (theoretical) is 7.6:1. In practice it is known to vary from 8.5:1 to 11:1.

If ammonia nitrogen is present in the water, chlorine reacts rapidly with it to form mono- and dichloramine. These compounds will appear in the combined residual. Depending upon the factors of concentration and ratio of chlorine to ammonia nitrogen, $NCl_3$ (nitrogen trichloride) may form, which causes an offensive odor at the tap. Chlorine reacts slowly with most organic nitrogen compounds to form organic chloramines which are stable even in the presence of high concentrations of free residual. Unfortunately these N-chloro compounds have little if any germidical power. Moreover, most of the N-chloro compounds impart objectionable off-flavors to the treated water, depending upon their concentration. These compounds make up part of the combined residual fraction, the other fraction is the free chlorine.

Fig. 6-7 illustrates the chlorine and ammonia reaction that produces the breakpoint phenomenon. At the breakpoint (bottom of the curve) there exists an irreducible minimum of total chlorine residual. These are called the "nuisance residuals." They consist of free chlorine, mono- and dicnloramine, and organochloramines. To the right of the dip there will be found increasing amounts of free residual together with the nuisance residuals and possibly some nitrogen trichloride. Nitrogen trichloride is not soluble in water, so it is extremely volatile. Therefore, water that generates nitrogen trichloride in the distribution system will produce an offensive odor at the instant of withdrawal from a tap. Reaction time between the chlorine and ammonia nitrogen is all-important. The only satisfactory way to provide proper control is to perform a bench scale study using different Cl:N ratios, different dosages, and different contact times. If the water tends to form $NCl_3$, try to find a contact time that occurs before the water leaves the plant, then the finished water can be subjected to postaeration, which readily removes any $NCl_3$. It is also readily destroyed by sunlight.

The success of the free residual process depends upon maintaining a free residual that is always at least 85 percent of the total residual, because free residual is taste free and is the most germicidal species.

The speed of reaction between chlorine and ammonia nitrogen to produce a free residual varies from water to water because this reaction is not only temperature

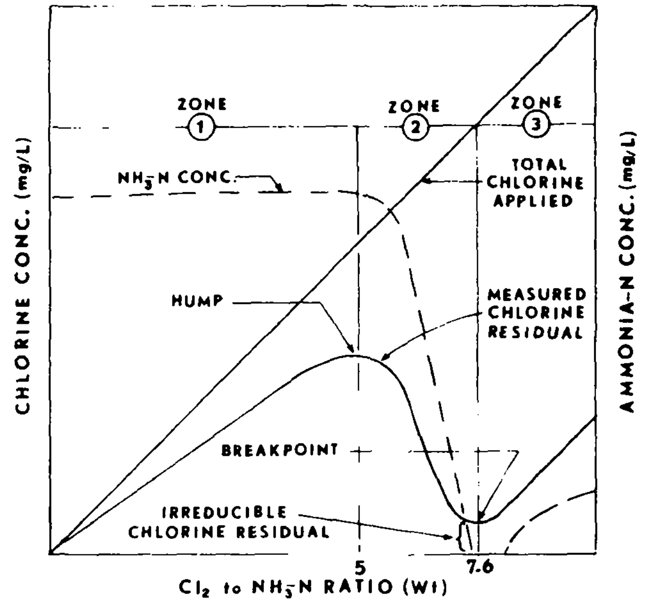


Fig 6-7 Effect of the chlorine and ammonia reaction illustrating the breakpoint phenomenon.

and *p*H dependent, it is grossly affected by the concentrations of both chlorine and ammonia-N. If organic nitrogen is present in the untreated water it compounds the problems associated with this process. This occurrence is described below.

**Effect of *p*H.** The free residual process is grossly affected by the *p*H of the water. This is due to the chemistry of hypochlorous acid (see Chapter 4). It dissociates in water as follows:

$$HOCl \longrightarrow H^+ + OCl^- \qquad (6\text{-}3)$$

All analytical techniques for measuring free residual include the sum of the undissociated hypochlorous acid (HOCl) and the hypochlorite ion ($OCl^-$). However the efficiency of the free residual process relates directly to the concentration of the undissociated HOCl. The reason for this lies in the fact that the germicidal efficiency of HOCl is believed to be about 100 times more than the $OCl^-$ ion.[100] The ratio of formation of each of these species is a function of *p*H (see Table 4-4, Chapter 4). For example, at *p*H 5 an aqueous solution of free chlorine contains 99.74 percent undissociated HOCl at 20°C. At *p*H 8 the undissociated HOCl is only 27.69 percent, the remainder is the $OCl^-$ ion. As can be seen from Table 4-4, dissociation is also affected by the temperature of the water but to a lesser extent.

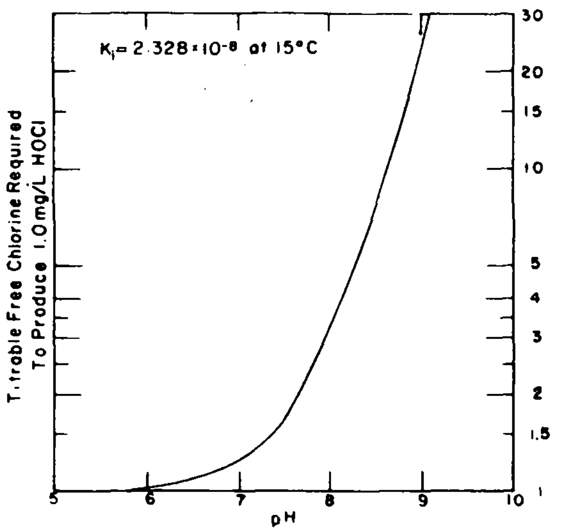


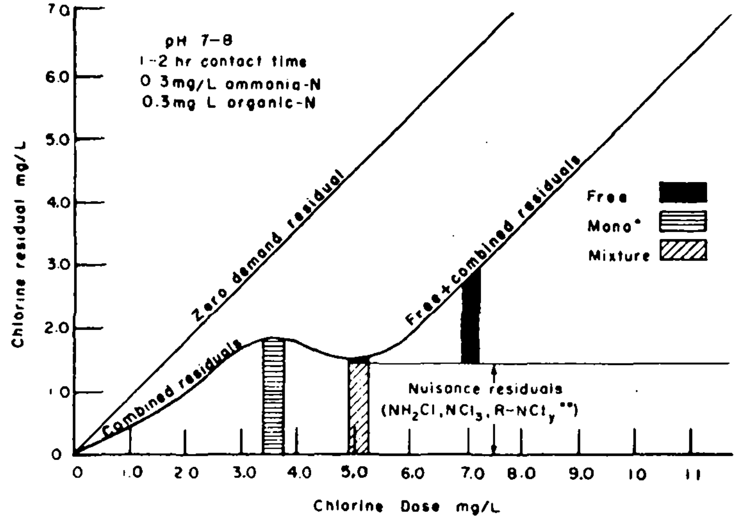
Fig 6-8 Effect of pH on the formation of hypochlorous acid.

Fig. 6-8 illustrates the amount of titrable free chlorine residual required to produce 1.0 mg/l HOCl. At *p*H 8 it requires 5 mg/l titrable free residual to produce 1 mg/l undissociated HOCl. If the *p*H were 7.5, only 2 mg/l of titrable free chlorine residual would be required to yield 1 mg/l HOCl, etc. The effect of *p*H on the free residual process affects the selection of chlorine dose as can be seen from the above example. Consider the example of virus destruction. It is generally conceded that a free chlorine residual is the most reliable for virus destruction. Clark et al.[124] believe that it takes about 0.3 mg/l of undissociated HOCl residual to inactivate Coxsackie A2 virus in about 20 minutes at 5°C.

If the *p*H of the water to be treated is 8.5 then 10 mg/l of titrable chlorine is required to produce 1.0 mg/l undissociated HOCl (see Fig. 6-8). The free chlorine residual required at this *p*H level will be 10 × 0.3 or 3 mg/l. This then is the minimum dose that will be required to provide 0.3 mg/l of 100 percent undissociated HOCl at the end of 20 minutes.[124,125]

Another consideration of the free residual process is the effect of sunlight on HOCl. While it is a relatively stable compound in that it resists loss due to aeration, losses due to bright sunlight have been reported as high as 2 mg/l HOCl in 4 hours. Chloramines act in reverse fashion; they do not suffer appreciable loss due to sunlight but are subject to losses as high as 15 percent of the residual by aeration. If nitrogen trichloride is present, all of it is quickly lost due to either sunlight or aeration or both.

**Reservoir Effect of OCl– Ion.** The notion is valid that at high *p*H values the distribution of the two species of titrable chlorine—HOCl and $OCl^-$—is such



*Predominantly monochloramine; $R\text{-}NCl_y$ titrates as dichloramine
**$R\text{-}NCl_y$ =organochloramines

Fig 6-9 Effect of chlorine-ammonia reaction in a water containing organic nitrogen.

that dissociation of the $OCl^-$ ion and the hydrogen ion provides a reservoir for the formation of HOCl. In accordance with Le Chatelier's principle,* as soon as the HOCl in Eq. (6-3) is used up, i.e., reduced to HCl, more HOCl is immediately formed from the $OCl^-$ ion and $H^+$ ion to maintain the chemical equilibrium in Eq. (6-3).

**Role of Organic Nitrogen.** Waters containing organic nitrogen in addition to ammonia nitrogen are quite another matter. Organic nitrogen in concentrations as low as 0.3 mg/l will seriously interfere with the chlorination process, and looms as a formidable obstacle in producing an acceptable water Two areas that have been troubled with the organic nitrogen problem are Little Falls, New Jersey[126] and Brantford, Ontario. The latter is well documented.[114,120] Griffin[104] found that waters high in albuminoid ammonia (organic nitrogen) displayed a plateau rather than the typical sharp dip associated with breakpoint curves. Fig. 6-9 illustrates this characteristic Palin[110] and others have confirmed these findings. In Chapter 4 Taras was able to clearly demonstrate how continuing chlorine demand tests could provide clues that can alert an operator to anticipate organic nitrogen problems derived from increasing pollution in the raw water supply.

The significant difference between ammonia nitrogen and organic nitrogen is

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* Le Chatelier's principle is defined as follows If some stress is brought to bear upon a system in equilibrium (such as the concentration of one or more of the components), a reaction occurs which displaces the equilibrium in the direction which tends to undo the effect of the stress.

the enormous varieties of organic nitrogen compounds that may occur in a water supply. When any of these are present in excess of 0.3 mg/l this will complicate the control of the free residual process. Each of these organic N compounds may have widely varying reaction times with chlorine to form organochloramines. The simple ammonia nitrogen compound ($NH_3$) reaction with chlorine rarely takes longer than 30 min for the complete destruction of the ammonia and a 75–80 percent loss of nitrogen. Depending upon the temperature this would be for an ammonia nitrogen concentration of 0.3–0.5 mg/l. However the reaction between chlorine and organic nitrogen may go on for days before going to completion with the chlorine.[120] Depending upon the particular nitrogen compound the reaction may never go to completion.[127]

Organic nitrogen in potable water is a direct result of wastewater contamination. However there is thought to be a significant amount entering surface supplies due to natural runoff that leaches and dissolves organic compounds from industrial waste dump sites. The source of most organic nitrogen compounds is in proteinaceous matter and urine, both of which are present in copious quantities in all domestic wastewater discharges. Urine contains substances that react with chlorine to form extremely stable N-chloro compounds that exhibit characteristics of dichloramine when differentiated by either the amperometric method or the DPD method of residual analysis. One of these constituents of urine is creatinine, which forms a chlor-creatinine compound and shows up on the curve of Fig. 6-9 as a nuisance residual. There are other N-chloro compounds (organic chloramines) in this same category that have little or no bactericidal value since they appear to be unreactive.[127] Their significance is not clearly understood, but the consensus is they are undesirable. In Fig. 6-9 it is to be noted that there is very little drop in the chlorine residual beyond the hump, signifying continuing and competing reactions between mono- and dichloramine, no perceptible loss of nitrogen in the reactions, and that the irreducible minimum residual is considerably larger than in water containing only ammonia nitrogen. Here again, it is the ratio of the free chlorine beyond the plateau to the total chlorine residual that is of importance. The combined fraction will contain N-chloro compounds responding to analysis as mostly dichloramine, and always some monochloramine. As the ratio of chlorine to nitrogen approaches 20:1, obnoxious quantities of nitrogen trichloride are certain to develop. Williams[113,114] has discovered that best results occur when enough chlorine is applied to produce a total of approximately 6.0 mg/l combined chlorine residual, resulting in about 5.0 mg/l free residual (HOCl), 0.4 mg/l monochloramine, and 0.6 mg/l dichloramine, as differentiated by the amperometric forward titration method. To prevent formation of nitrogen trichloride in the distribution system, this water is subsequently treated with an excess of ammonia to convert the outgoing residual to monochloramine 80 percent and dichloramine 20 percent. The water can be dechlorinated and rechlorinated, whichever makes the most palatable water at the least cost.

Another important factor in the kinetics of chlorine and nitrogenous compounds is the relationship of monochloramine to organochloramines. In water reuse systems where contact times can be monitored and are designed for maximum effectiveness, it has been discovered that, after a certain point, as the contact time is lengthened the germicidal efficiency starts to decrease. This phenomenon seems to occur when the contact time exceeds one hour—at least in some systems. In these particular systems it was discovered that the combined residual showed a decrease in the monochloramine fraction and a simultaneous increase in the dichloramine fraction which is suspected of being ineffective organochloramines. Therefore it appears that given time, monochloramine will be gradually converted to organochloramines.

Whenever organic nitrogen is present in concentrations higher than 0.3–0.5 mg/l the operator can expect difficulties with the free residual chlorination process. This much organic nitrogen indicates a highly undesirable low-quality water with recent heavy sewage contamination. Special pretreatment processes should be considered for these waters. White has suggested that a water quality parameter for any potential drinking water supply be limited to 0.3 mg/l organic N.[128]

**Formation of Potentially Hazardous Compounds.** The 1970s witnessed the first serious indictment of the free chlorine residual process. This discovery was the consequence of the U.S. Public Health Service concern over the widespread use of herbicides, pesticides and other petrochemical products. They feared the intrusion of these organic chemicals into the water supplies. A 1970 survey discovered that the levels of dissolved organics in many water supplies exceeded the Public Health Service's recommended limit for carbon chloroform extractable organics, which at that time was 200 micrograms per liter.[129] In 1972, the EPA reported that 46 organic chemicals were present in trace amounts in both the raw and finished water supplies at three locations along the Lower Mississippi,[130] and a 1974 EPA study identified 66 organic compounds in the New Orleans drinking water.[131] On the same day that the New Orleans report was issued (Friday, Nov. 8, 1974), Russell E. Train, Administrator of the EPA, announced that he was ordering an immediate nationwide survey to determine the concentration and potential health effects of certain organic chemicals in drinking water.

On December 16, 1974 President Ford signed into law, Public Law 93–523, The Safe Drinking Water Act. Section 1442(a)(9) of this Act states:

> The Administrator shall conduct a comprehensive study of public water supplies and drinking water sources to determine the nature, extent, sources of, and control of contamination by chemicals or other substances suspected of being carcinogenic. Not later than 6 months after the enactment of this title, he shall transmit to Congress the initial results of such study together with such recommendations for further review and corrective action as he deems appropriate.

Then on Dec. 18, 1974, Administrator Train named the 80 cities to be included in the National Organics Reconnaissance Survey.

The issue of chlorinated organics formed in the treatment of drinking water became a priority topic to the U.S. EPA beginning in January, 1975. In 1974 the work of Rook[132] in the Netherlands and Bellar, Lichtenberg, and Kroner,[133] in the U.S.A. demonstrated that chlorine used for disinfection did *in some waters* react with organic precursors to produce some trihalomethanes (mostly chloroform) in the finished water which were not found in the respective raw water at the locations of study. This was indeed an unsettling observation. To assess the general situation across the United States, the National Organics Reconnaissance Survey was conducted in 1975 by Symons et al.[134]

This survey revealed that four trihalomethanes (THMs): chloroform (trichloromethane, $CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform (tribromomethane, $CHBr_3$) are widespread in chlorinated drinking water in the U.S.A. Table 6-2 shows the THM concentration in water supplies of heavily populated areas picked at random from the NORS report described above.[134] There are only three metropolitan areas that exceed the EPA interim maximum contaminated level.

A review of the current knowledge of trihalomethane formation by Trussell and Umphries is an informative document.[135] It discusses in detail the chemistry of the formation of chloroform by chlorine and the chemical path of bromoform formation by the reaction of chlorine with the bromide ion.[136]

Chloroform, which seems to be present in the greatest concentration of the four THMs detected, is a known carcinogen to animals and is therefore of immediate concern. However it is not considered an acute hazard to man, particularly at the low concentrations detected. Nevertheless it became clear that chlorination practices should be reviewed in order to minimize THM formation.

Morris et al.[137] reported in 1980 that a large number of nitrogenous organic compounds occur naturally in water supplies and react readily with aqueous chlorine. This results in the formation of N-chloro compounds that exert a significant chlorine demand and some can produce chloroform, particularly in the *p*H range of 8.5–10.5. The compounds identified by Morris et al, are adenine, 5-chlorouracil, cytosine, guanine, purine, thymine, and uracil.

This same investigation also revealed that summer blooms of blue-green algae can result in a significant increase in the organic N content of a potable water supply. This raises concern about the potability of a finished water during occurrences of summer blue-green algae. Aside from the taste and odors associated with such occurrences, high levels of organic N material released by these algae, could result in increased THM formation as well as combined N-chloro species that demonstrate little or no germicidal value. Moreover some of these N-chloro compounds yield false positive free chlorine residuals.*

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* The precise level of interference is not known. The amperometric titration method seems to demonstrate the least interference from the N-chloro compounds in the measurement of free chlorine. Morris et al[137] indicated the interference for some compounds was less than 0.5 mg/l residual and some were slightly more.

Table 6-2 Total THM Concentration in Treated Water from a Selected List of Metropolitan Areas from NORS Report[134]

| *Water Supply and Raw Water Source* | *TTHM, μg/l* |
|---|---|
| Boston, Mass<br>Norumbego Treatment Sta. | 4.8 |
| New York City<br>Croton Reservoir | 29.9 |
| Little Falls, NJ<br>Passaic Valley Water Co<br>Passaic River | 71 |
| Philadelphia Water Dept<br>Torresdale Plant<br>Delaware River | 106 |
| Washington DC<br>Dalecarlia Plant<br>Potomac River | 51.2 |
| Baltimore, MD<br>Loch Haven Reservoir<br>Montebello Plant No. 1 | 45 |
| Fairfax Co. Water Authority<br>Anandale, Virginia<br>New Lorton Plant<br>Occoquan River Impoundment | 73.5 |
| Miami, FL<br>Preston Plant<br>Groundwater | 427 |
| Ottumwa, IA<br>Des Moines River | 0.8 |
| St. Louis, MO<br>Central Plant<br>Missouri River | 72.2 |
| Denver CO<br>Marston Plant<br>Marston Lake | 27 |
| Cape Girardeau, MO<br>Mississippi River | 141.3 |
| Salt Lake City, UT<br>Mountain Dell Res. | 42 |
| Phoenix, AZ<br>Verde Plant<br>Salt & Verde Rivers | 44 |
| Calif. Water Project<br>California Aqueduct<br>Sacramento & San Joaquin Riv. | 50 |
| Concord, CA<br>Contra Costa Co. Water Dist.<br>Calif. Water Proj. & San Joaquin Riv.<br>Bollman Plant | 55.8 |
| Atlanta GA<br>Chattahoochee River Plant | 48 |
| Chattanooga, TN<br>Chattanooga River | 40 |
| Nashville TN<br>Lawrence Plant<br>Cumberland River | 21.3 |
| Cincinnati, OH<br>Ohio River | 62.3 |
| Chicago, IL<br>So. District Filter Plant | 29.3 |
| Indianapolis, IN<br>White Riv. Plant & Wells<br>White River | 42 |
| Detroit, MI<br>Waterworks Park Plant<br>Detroit River at Belle Isle | 24.4 |
| Milwaukee, WI<br>Howard Ave. Plant<br>Lake Michigan | 19.1 |
| Dallas, TX<br>Bachman Plant<br>Trinity River, Elm Fork | 23 |
| Los Angeles, CA<br>Owens River Aqueduct | 51 |
| San Diego, CA<br>Miramar Plant<br>Colorado River Aqueduct | 104 |
| San Francisco, CA<br>O'Shaugnessy Lake<br>Yosemite Calif.<br>San Andreas Filter Plant | 60.6 |
| Seattle WA<br>Cedar River System | 15.9 |
| Cleveland, OH<br>Division St. Filter Plant | 31 |

The EPA generated many investigations at several treatment plants in the hopes of modifying the chlorination process towards the reduction of THMs. It was found among other things, that it was the presence of free chlorine (HOCl) which enhanced the formation of chloroform. It was also found that the THM formation was as much a result of the organic content of the water as it was the result of the chlorine being used. It was also confirmed that neither ozone, chlorine dioxide nor chloramines contributed to the formation of THMs.

In 1978, the EPA set maximum concentration limits on various compounds in potable water. Chloroform formation was given a maximum concentration level (MCL) of 100/$\mu$g/l. A dosage limit for chlorine dioxide of 1.0 mg/l was suggested and it was stipulated that chloramines could only be used as a secondary disinfectant.[99] The EPA stance on chloramines changed in the 1980s; see the section on the "Ammonia–Chlorine Process" in this chapter.

In 1977, the EPA published a state of the art report on the use of ozone, chlorine dioxide and chloramines as alternatives to chlorine for disinfection of potable water.[138] These studies are discussed for chlorine dioxide in Chapter 12 and for ozone in Chapter 13.

## Control and Removal of Trihalomethanes

**Current Control Strategies.** In spite of the fact that free chlorine can in some instances produce unacceptable concentrations of THMs there are a great many waters that remain either unaffected or are amenable to simple procedures such as moving the point of application or reducing the chlorine dosage.

The generation of THMs by chlorine is related to the precursors such as humic and fulvic acids, and a variety of organics. The quality and quantity of precursors is in turn related to the chlorine demand of the water which reflects upon the quality of the untreated water. This is why a continuous record of the chlorine demand of the untreated water is so valuable in evaluating any change in water quality.

Since THM formation is time dependent, some water systems follow free residual chlorination with ammonia application after some specified contact time with the free chlorine.[139] The time interval between the chlorine–ammonia sequence is usually on the order of 10–20 min. This utilizes the germicidal efficiency of HOCl, while the ammonia inhibits the formation of THMs. Moreover postammoniation has been practiced for many years for quality control in the distribution system.

Barnett and Trussell[140] reported in 1978 their investigation of THM formation in the Casitas, California, water system. They found a wide seasonal fluctuation in the total organic carbon (TOC) and potential THM content in the raw water supply (Lake Casitas). They found that THM levels can be maintained within acceptable limits by either adding ammonia downstream from the first point of chlorine application or by free chlorine followed by activated carbon filtration and that TOC content and THM precursors can be reduced significantly by adding 2 mg/l ozone prior to chlorination. Rook[141] reported in 1976 on the removal and prevention of haloform formation that the combination of ozone (8 mg/l) followed in two minutes by chlorine (7 mg/l) is an effective way to remove the fulvic acid precursor. He found that anion exchange resins following coagulation, sedimentation, and filtration is effective but relatively expensive for the removal of organic precursors. Rook also reported that the removal of haloforms generated during chlorination was accomplished by activated carbon or air stripping. The carbon method was disappointing because the haloforms broke through after only two to three weeks operation.

Aeration is effective in reducing chloroform since it is a volatile compound. Some investigators have reported removals better than 95 percent[142] when using an ammonia stripping tower at *p*H 11, while others can do no better than 50–55 percent using a countercurrent flow aerator.[143]

Absorption by either powdered activated carbon or granular activated carbon (GAC) filters will remove THMs. The powdered form of carbon is not an attractive choice because huge doses (50–60 mg/l) are usually required, which in addition to being expensive, create a sludge problem.[150] In 1981 Anderson et al.[144] examined the feasibility of trace organics control with a specially formulated powdered activated carbon, at dosages considerably less than previously reported. THM formation levels were reduced more than 50 percent. A new ruling by the EPA in March 1982 will allow the use of PAC as an accepted technology provided its use is intermittent or seasonal at dosages not to exceed 10 mg/l on an annual average basis.

Granular activated carbon (GAC) and biologically activated carbon (BAC) have been investigated for both precursor removal and TTHM (Total THM) removal. Carbon is effective, but has a low reliability factor. In TTHM removal, chloroform invariably breaks through in two to three weeks. BAC is discussed in Chapter 13. GAC has been the subject of many investigations.[145-149]

The most overpowering objection to GAC is the cost. In 1980–81 the Metropolitan Water District of Southern California hired James M. Montgomery Engineers to make a comprehensive investigation that scrutinized all of the possible alternatives to control the formation of THMs and/or to remove their precursors. This project was a joint effort between the client and the Engineers.[151] During this investigation pilot plant studies demonstrated that GAC was 100 times more expensive than chloramines. For various valid reasons all of the many alternative methods studied were discarded in favor of chloramines.

Sometime in 1981 the American Water Works Association filed a lawsuit against the U.S. EPA which challenged the EPA standard of 100 micrograms per liter for total trihalomethanes (TTHM). This suit was settled in March 1982. The EPA made two important changes which represented a victory for AWWA. First, chloramines were raised to alternate primary disinfectant status and second, the GAC filtration and BAC (biologically activated carbon) filtration technologies as requirements were eliminated in order to obtain a variance under the proposed new rules by the EPA.[152]

A report similar to the one developed for MWD of Southern California was completed in 1982 by Kennedy Jenks Engineers for the Alameda (California) County Water District. This investigation concluded that treatment with chloramines was the best alternative.[153] Others who have already switched from free chlorine to chloramines have reported successful control of THMs and equally successful water quality control.[154,155]

**Max THM Potential.** The potential for the formation of THMs is directly related to the chlorine demand. Trihalomethanes are formed by the reactions between natural organic compounds (humic and fulvic acids) in the environment, naturally occurring bromides, and chlorine used in the water treatment processes. One of the techniques to determine the potential THM formation is a procedure long known as the "chlorine demand" of a water.

In the case of THM formation the recommended procedure is to add sufficient chlorine to the sample so that a measurable free chlorine residual will persist for at least seven days. The samples should be stored in screw-top or crimp-top bottles filled to exclude air space and placed in a 25°C water bath in the dark. Depending upon local circumstances the detention time may be more or less than seven days.[156]

The total trihalomethane (TTHM) concentration is measured at daily intervals. These concentrations are then plotted to generate a TTHM curve as shown on Fig. 6-10. When the curve reaches a plateau that is the maximum THM potential (MTP).

This extended chlorine demand test can serve as a useful tool for the water producer. It is a significant water quality parameter that should be evaluated annually. To make use of Taras' chlorine demand concept described in Chapter 4, chlorine residuals should be measured after 30 min and 60 min contact time and then at hourly intervals for the first 24 hours.

Each water supply will react differently to this test. Chlorine dosages to provide a measurable free chlorine residual to produce a plateau will vary from 2 to 20 mg/l and the reaction time may take from 5 to 15 days. These variations will be a function of the water quality and the nature and concentration of the precursors.

**Chlorine Demand.** There is sufficient data from more than fifty years of operating experience to declare that the 15 minute chlorine demand of a raw water be used as a surrogate parameter for water quality. It would be proposed then that if the chlorine consumed in this 15-min period exceeded the arbitrary allowable level, the water in question would have to undergo some pretreatment process to reduce the natural chlorine demand to the acceptable level.

To put the chlorine demand level in perspective it is important to mention that the source of all the water on this planet—seawater—has a 15-min chlorine

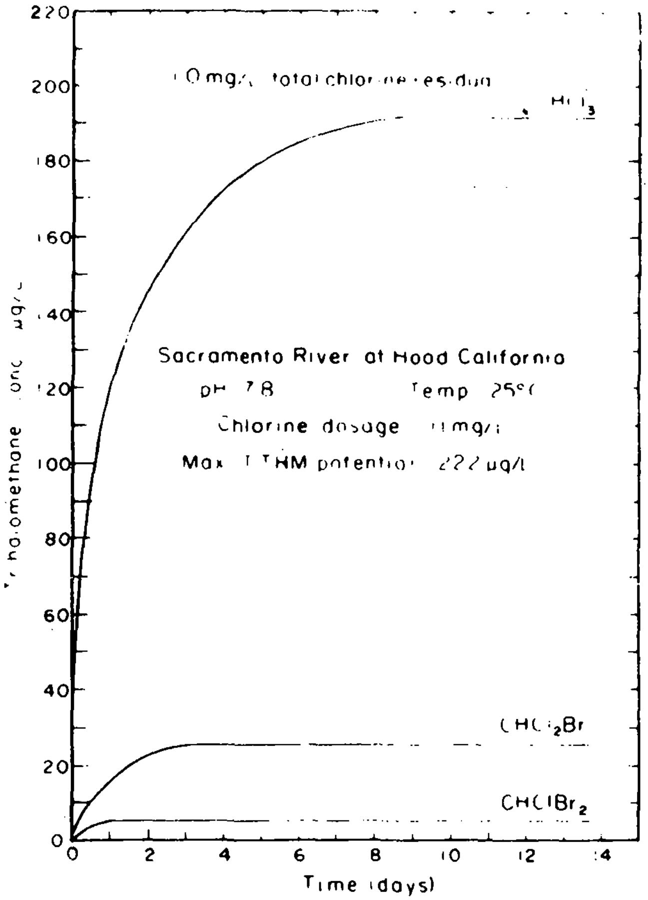

Fig 6-10 Total trihalomethane formation potential due to the free residual process[156]

demand that rarely exceeds 1.5 mg/l. White suggests the maximum allowable raw water chlorine demand should not exceed 2 mg/l.

## CURRENT PRACTICES IN THE U.S.A.

### Review of Modern Practices

**Chlorine Dosages.** In March 1978 a questionnaire developed by the AWWA Disinfection Committee was mailed to numerous water utilities in an attempt to document current practices.* There were some 350 respondents to this questionnaire.

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* This questionnaire was under the leadership of Geo. Clifford White, chairman of the committee.

The respondents indicated that the points of application could be a combination of any of the following

- Pre raw water storage
- Precoagulation/post raw water storage
- Presedimentation/postcoagulation
- Postsedimentation/prefiltration
- Postfiltration (disinfection)
- Distribution system (disinfection/water quality)

The chlorine dosage range reported was a minimum of 0.2 mg/l to a maximum of 40 mg/l The maximum dosage reported by 96 percent of the respondents was 15 mg/l The all time record is 120 mg/l reported at Ottumwa, Iowa in 1950 [illegible] The raw water was from the Des Moines River This range of dosages demonstrates dramatically the variation in water quality throughout North America When practicing the free residual process, winter ice cover on surface supplies will almost automatically double the summertime chlorine demand. This is a result in the ammonia N increase due to the ice cover

To combat pollution and taste and odor problems various combinations and dosages of chemicals are in use today in both the U.S. and Canada. These include combinations of chlorine and chlorine dioxide, ammonia, potassium permanganate, and activated carbon, sometimes followed by dechlorination with either sulfur dioxide or carbon

Prechlorination of low quality water is most often the operator's salvation. It is one of the most important tools for maintaining the efficiency of a water treatment plant In these situations, which are numerous, it would be virtually impossible to turn out an acceptable water if it were not for the unique ability of chlorine to maintain a persisting residual throughout the process. In these cases disinfection is just a side effect However a lot of these water suppliers will have to reevaluate the chlorination process in order to meet mandatory TTHM regulations.

Two examples of low quality water that require chlorine dosages up to 16.0 mg/l are the Grand River at Brantford, Ontario, Canada[159] and the Passaic River at Little Falls, New Jersey [160]

In North America, poor quality water has been treated for decades by a prechlorination dose sufficient to provide a substantial free residual in the flocculation or sedimentation basins Many of these plants follow this by an intermediate dose of chlorine or chlorine dioxide sufficient to carry a residual through the filters. This practice will certainly have to be modified in some instances. Switching from free residual chlorine to chloramines or chlorine dioxide might be the answer in some cases Other cases might need to change the entire pretreatment processes, which could include ozone (See Chapter 13 )

In those cases where free residuals through the treatment plant do not generate objectionable levels of THMs in the finished water, postammoniation to convert the free chlorine to chloramines can be beneficial. This has been practiced at Brantford Ontario and other plants for decades.

Dechlorination by sulfur dioxide to trim the chlorine residual as it enters the distribution system is being practiced in many places.

The case of clean waters where chlorine is used solely for disinfection is remarkably different from low quality waters. Two typical examples are the supplies for the City of San Francisco and the East Bay Communities in Alameda and Contra Costa counties in California. These waters are derived directly from melted snow in separate runoff areas high in the Sierra Nevada mountains. The San Francisco supply is transported by a 165-mile aqueduct and the East Bay supply travels about 90 miles to various local storage reservoirs. The chlorine dosage required for disinfecting these waters is 0.8 1.2 mg/l The San Francisco supply was plagued from the start by assorted difficulties. The most humiliating one occurred a few months after the system was put in operation. Part of the 165 mile aqueduct consists of a concrete lined tunnel 25 miles long through the Coast Range mountains. Although the concrete tunnel lining is up to 12 inches thick, many cracks developed due to heavy ground caused by groundwater. The groundwater is laden with filamentous bacteria (*Crenothrix*) which infiltrates the tunnel and gives rise to luxuriant growths on the tunnel lining. This created a debacle in the distribution system. Industries were forced to shut down because of this biofouling and the sloughing of the filamentous debris. To combat the problem, the city of San Francisco, after having investigated several treatment methods, concluded that a persistent chlorine residual was the only answer. Therefore a chloramine station was built (1937) to inject chlorine and anhydrous ammonia at the entrance to the tunnel. A 1.5 mg/l dose produced a combined residual of about 1.0 mg/l at the end of the tunnel 25 miles away. When ammonia became difficult to get during World War II the system was converted to the free residual process which is still in use (1983). San Francisco water does not generate THMs above the EPA minimum contamination limits.

There are many areas in the U.S.A. which are not as fortunate as the San Francisco Bay Area. Two of these are St. Louis and Kansas City, Missouri: St. Louis, using Mississippi River water, prechlorinates at an average 5 mg/l. This is supplemented by intermediate doses of chlorine to preserve the efficiency of the filter system. Kansas City, using Missouri River water, prechlorinates at about 12 mg/l. These chlorine applications are not for disinfection. This is to keep the water treatment processes from deteriorating and for taste and odor control.[161]

The City of Chicago, using a cleaned up Lake Michigan water, prechlorinates at only 1 1.2 mg/l. This is comparable to the melted snow waters of California. This prechlorination dose is designed to provide an absolute minimum of 0.25 mg/l free chlorine through the filters. It is supplemented by a postchlorination dose of 0.25 0.5 mg/l to give a 0.75 mg/l free chlorine residual entering the distribution system. To exemplify the effect of pollution on chlorination, whenever there is an upset with the Chicago Ship Canal, amounting to a reversal of flow which dumps canal water into Lake Michigan the chlorine demand escalates to 10 mg/l, and even at this dosage there is so much $NH_3$-N in the raw water that a free chlorine residual is not attainable.[162]

Surface waters in some areas of Pennsylvania require prechlorination doses of 7.8 mg/l and the City of Philadelphia provides sufficient chlorination equipment capacity to dose as high as 30 mg/l at the raw water basin outlet (ice cover situation) and up to 4 mg/l chlorine dioxide for pretreatment.[161]

It is significant to note the quality of the water which is provided by the billion dollar California Water Plan. This water is a mixture of several rivers, primarily the Sacramento and San Joaquin. This water requires only 2.4 mg/l prechlorination dose to produce a 0.7 mg/l free residual in the filter plant finished water without any intermediate chlorination. This is a tribute to the diligence and surveillance of both the California State Department of Health and the California Water Resources Quality Control Board for their programs designed to preserve the water quality of the receiving waters.

**Chlorine Residuals.** To this question there were 226 respondents to the AWWA Disinfection Committee Questionnaire.[84] The highest reported was 5 mg/l and the mean was 1.4 mg/l (total Cl). The figures for free residuals were about the same: maximum 4.75 mg/l and mean 1.0 mg/l.

Out of 332 respondents, 235 were using DPD, 165 amperometric titrator, 127 acid O-T, 11 neutral O-T, 1 FACTS, and 1 starch-iodide.

**Contact Time.** One of the questions asked in this questionnaire was designed to determine the contact time between the point of application of chlorine and the first consumer. Strange as it seems, 90 percent reported 10 hours, while 6 percent reported 2 minutes. The median was 60 min, while the mean was 237 min.

**Chlorine Demand.** Chlorine demand tests reportedly take place in about 40 percent of the respondents facilities. Twenty of the utilities reported maximum demands between 5 and 10 mg/l chlorine, and another 11 reported demands between 10 and 22 mg/l. Of 123 respondents the median demand was 1.8 mg/l. However the maximum reported was 65 mg/l at a maximum contact time of 12 hours.

## Deficiencies in Current Practices

**The Community Water System Survey.** The most significant information available on the production of potable water in the U.S. is the Community Water System Survey of 1970.[129] This survey points directly to the deficiencies in current practices. As is always the case, whether it be potable water or wastewater treatment, it is the small communities and the small producers who have the greatest deficiencies. The large producers are endowed with more sophisticated treatment techniques, adequate funding, and more qualified operating personnel This report reveals that in communities of less than 500 population, only 50 percent met the Drinking Water Standards of 1962 (USPHS). At the same time in communities of 100,000 or larger, 73 percent met these standards. Of equal or greater significance the survey revealed that 19 percent of surface and mixed-source water not practicing disinfection were not properly protected at the source, and of those facilities practicing disinfection, 16 percent were inadequate and 7 percent had inadequate control of the disinfection process. Overall, this survey indicates that too many Americans are not being provided with potable water that meets contemporary standards of good practice.

Too many unnecessary risks are being taken in the production and distribution of potable water, particularly those small but numerous water systems, e.g., ski and other resorts, roadside restaurants, bus stops, motorway rest areas, trailer camps, farms, suburban homes, isolated institutions, organized summer camps, and other similar small water systems. Many of these small supplies are pumped into a pressure tank and thence to a close-coupled distribution system with practically zero contact time. Obviously the only line of defense for these systems is the disinfection facility. Therefore, this facility must be designed with a proper factor of safety to allow for variation in water-quality parameters affecting disinfection. The same rationale would also hold true for large systems under similar circumstances.[165]

**Viruses.** One of the major causes for concern is that the frequency of viral diseases and acute gastrointestinal illnesses (AGI) has been on the rise in the past four decades, while typhoid has almost disappeared in the U.S.A. Until 1971 gastroenteritis as such was not a reportable disease. Since 1971 the EPA and CDC have entered into a cooperative reporting scheme classifying such illnesses along with other outbreaks of known etiology. This has gone a long way in solving the origin of these outbreaks. During the period 1961 1970 a total of 26,546 cases of gastroenteritis were definitely attributed to water.[166] Of 52 waterborne outbreaks in the U.S.A. in 1971–72 there were 22 outbreaks of AGI amounting to 5615 from a total of 6817 cases of all waterborne illnesses.[167] The concern here is that these cases may all be of viral origin. See the section on "Viral Diseases" in this chapter There are over 100 viruses excreted in the feces of man which have been reported to be in contaminated water. Any of these could cause a waterborne disease and some have done so.

In order to cope with viruses, the disinfection process will have to address itself to longer minimum contact times and higher residuals. Surface waters that rely solely on disinfection will have to be reevaluated. In these cases it may be necessary to adopt filtration as an additional barrier.

**Proof of Disinfection.** To date we have been relying upon the coliform group of organisms as proof of disinfection. So far this indicator has served us well for bacterial infection. However it cannot be relied upon as an indicator for viral infection. Microbiologists are in total agreement that there is no observed relation between total coliforms, fecal coliforms, or standard plate counts and the presence of viruses. Also there is no observed relation between the detection of *Salmonella* and viruses and vice versa. With our present knowledge of viruses, the coliphages or enteroviruses cannot be used as indicators. This means that proof of disinfection must derive from a properly treated water; this would involve filtration and the assurance of substantial chlorine residual in the distribution system. It has been demonstrated that water treatment processes such as those used to treat Missouri River water downstream from Kansas City, where fecal coliform densities are as high as 16,000 per 100 ml, are a reliable barrier for viruses.[55] This investigation was unable to isolate any viruses in the treated water.

Sanitary biologists have expressed dissatisfaction with coliforms as indicator organisms for more than a decade. They insist that this group of organisms is not resistant enough to chlorine or other disinfectants to allow any factor of safety. There have been many cases of enteric organisms such as the genera *Klebsiella* and *Enterobacter* (*cloacae*) found responsible for positive samples occurring in the routine coliform sampling procedure. The discovery of such potentially hazardous organisms in a distribution system is unsettling, particularly when the water has been coagulated, settled, filtered, and chlorinated sufficiently to carry a residual (0.5 mg/l) throughout the distribution system. There have been cases where the residual was kept much higher in an attempt to destroy these organisms, but without complete success. It is thought that these encapsulated organisms, once they are in the distribution system, may be harbored in protective slime, scale, or sediment. The *Klebsiella* germs are encapsulated organisms and can cause severe enteritis in children. In adults they can cause pneumonia and upper respiratory tract infections, septicemia meningitis, peritonitis, and urinary tract infections. *E. cloacae* present in a water system implies that there could be contamination of fecal origin. *E. cloacae* is not known to have caused any waterborne disease. However, *Klebsiella* is a hazardous organism.[169]

In view of the above, the work of Engelbrecht et al. is of considerable importance.[168] Their investigation evaluates two promising groups of organisms. These include two acid-fast cultures, *Mycobacterium fortuitum* and *M. phlei*, and a yeast, *Candida parapsilosis*. The resistance of these two groups of organisms to chlorine is believed to be in the range necessary to inactivate both bacillary pathogens and waterborne viruses. Further research for a better indicator organism is recommended.

The precise reason why *Klebsiella* and *E. cloacae* can be isolated in distribution systems in the presence of a significant free chlorine residual after the water has been coagulated, settled, filtered, and disinfected remains a mystery. In this chapter, under "Distribution System," some probable causes are discussed.

In spite of the above anomalies it is still the consensus that the best method of assuring the microbiological safety of drinking water is to maintain good clarity, provide adequate disinfection (which includes maintenance of a disinfectant residual in the distribution system), and make frequent measurement of the total coliform density and general bacterial population (SPC) in the distributed water.[174] The emphasis is always on a persisting disinfectant residual in the distribution system.[173,174] The Community Water Supply Study[164] undertaken in 1969 to investigate the status of the surveillance program in each of 969 water supply systems found that only 10 percent met the sampling criteria, whereas 90 percent either did not collect sufficient samples or collected samples that showed poor bacterial quality or both. In general the survey showed that the probability of finding coliform bacteria in a distribution system decreases as the residual chlorine increases. Overall the Community Survey specifically showed that in chlorinated water supplies a chlorine residual must be maintained throughout the distribution system in order to have confidence that disinfection has been accomplished.

Robeck[174] has been able to demonstrate with data that when properly used, the chlorine residual test satisfies the problems occurring with bacteriological sampling. The sampling problems in many utilities occur when there is too high a proportion of the sampling in the free flowing high turnover area of a system, and too small a percentage in the troublesome areas: reservoirs, dead ends, and low flow areas.

It could be concluded then that the safest drinking water system is one that maintains an adequate chlorine residual throughout the distribution system which is verified by frequent sampling or continuous residual monitoring. This notion presupposes that this water meets the turbidity standards as well.

## OBJECTIVES OF CHLORINATION

### Disinfection Guidelines

**Free Residual Process.** Disinfection practices should be governed by the chlorine residual contact time envelope, based upon the destruction of a consensus organism.[176] This concept was first proposed by Baumann and Ludwig in 1962.[175] The major factors affecting the germicidal efficiency of the free residual process are chlorine residual concentration, contact time, *p*H, and water temperature. Increasing the chlorine residual, the contact time, or the water temperature increases the germicidal efficiency. Increasing the *p*H above 7.5 drastically decreases the germicidal efficiency of free chlorine. (See Chapter 4.)

A review of the literature shows the resistance of pathogens to free residual chlorination varies over a wide spectrum of organisms. Most of the viral pathogens are considerably more resistant than the bacterial pathogens. Cysts in most instances are the most resistant to free chlorine. Varma and Baumann compiled the chlorine residuals and contact times needed to kill vegetative bacteria, viruses and amoebic cysts from a comprehensive review of the literature.[76] From this review they plotted the available data shown graphically in Fig. 6.11 for the chlorine concentra-

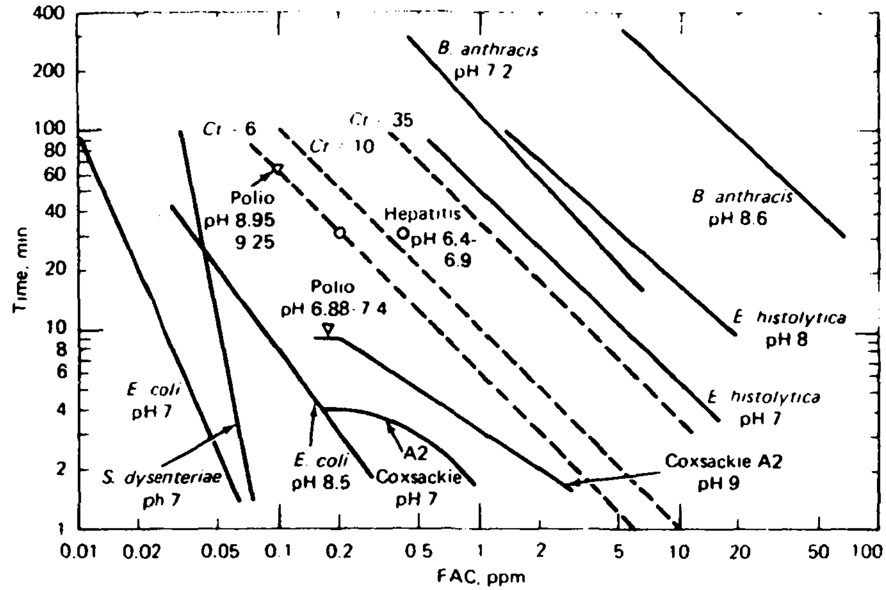

Fig 6-11 Disinfection versus free available chlorine residuals (Time scale is for 99.6 to 100 percent kill. Temperature was in the range of 20 to 29°C, with pH as indicated.) Reprinted from *Journal American Water Works Association* **54**, 1379, Nov 1962, by permission of the Association

tion–contact time relationship to achieve the destruction of these four classes of organisms. Table 6-3 shows the source of the data for the plots in Fig. 6-11 which were considered to be the most up-to-date and reliable. Fig. 6-12 represents the plot of disinfection versus free chlorine residuals at 0 to 5°C as compared to Fig. 6-11 which is at a temperature range of 20 to 29°C. Since there are many locales where the minimum water temperature for both well water supplies and surface waters may never fall as low as 0°C, Baumann and Ludwig[175] constructed Fig. 6-13 which represents a transposition of the plots on Fig. 6-11 at 20 to 29°C and Fig. 6-12 at 0 to 5°C to a plot representing a water temperature of 10°C. This transposition was accomplished by means of the Van't Hoff–Arrhenius reaction rate equation:

$$\log_e \frac{t_1}{t_2} = \frac{E(T_2 - T_1)}{R\, T_1\, T_2} \qquad (6\text{-}4)$$

in which $T_1$, $T_2$ = upper and lower temperatures between which reaction rates are compared. $t_1$, $t_2$ = times in minutes required for equal percentage of kill to be effected at temperatures $T_1$ and $T_2$ at a fixed concentration of disinfectant. $E$ = activation energy (calories). $R$ = gas constant, 1.99 cal/°K, 10°C = 283°K.

## Table 6-3 Sources of Data for Disinfection Time—Chlorine Concentration

| *Organism* | *0°C Temp. Range* | *pH* | *Source* |
|---|---|---|---|
| *E. coli* | 2–5 | 7, 8.5 | Butterfield[177] |
| *E. coli* | 20–25 | 7, 8.5 | Butterfield[177] |
| *Salm. typhosa* | 20–25 | 9.8 | Butterfield[177] |
| *S. dysenteriae* | 20–25 | 7.0 | Butterfield[177] |
| Poliomyelitis | 20–30 | 6.85–9.25 | Lensen[178] |
| Poliomyelitis | 0 | 7, 8.5 | Weidenkopf[179] |
| Coxsackie A2 | 3–6 | 7–9 | Clark and Kabler[180] |
| Coxsackie A2 | 27–29 | 7–9 | Clark and Kabler[180] |
| *E. histolytica* | 3 | 7, 8 | Fair[181] |
| *E. histolytica* | 20–25 | 7, 8 | Snow[182] |
| *B. anthracis* | 4 | 7.2, 8.6 | Brazis[183] |
| *B. anthracis* | 22 | 7.2, 8.6 | Brazis[183] |
| *P. tularensis* | 15.5–18.5 | 7.3 | Foote[51] |
| Hepatitis | room | 6.4–6.9 | Neefe[184] |

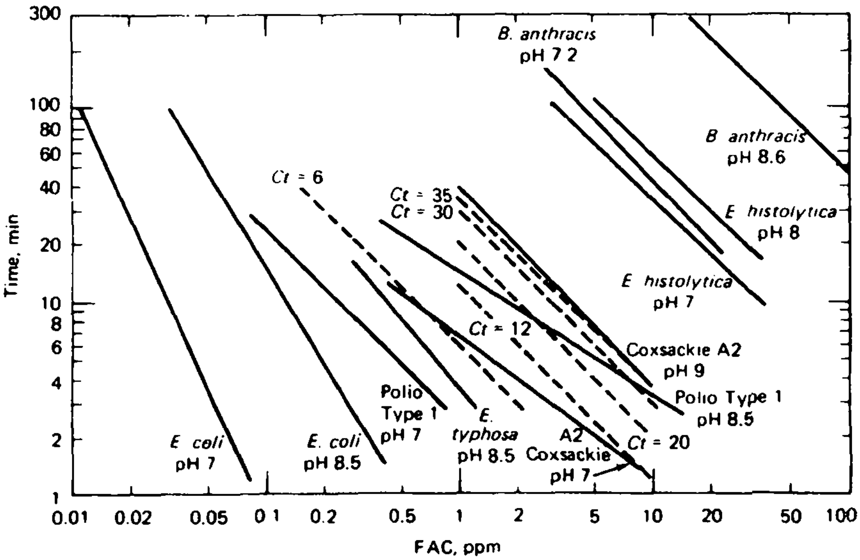

Fig 6-12 Disinfection versus free available chlorine residuals. (Time scale is for 99.6 to 100 percent kill. Temperature was in the range of 0 to 5°C, with pH as indicated.) Reprinted from *Journal American Water Works Association* **54**, 1379, Nov 1962, by permission of the Association

The result of the application of this mathematical transformation procedure is Fig. 6-13.

The curves illustrated in Figs. 6-11, 6-12 and 6-13 are plotted on log-log paper to give straight lines. These lines follow the general equation $y = ax^b$, where $b$ is the slope. Since $b$ is negative, the curve is hyperbolic. The curves shown in solid lines have slopes that approximate $-1$. If $y$ is plotted as time $t$, and $x$ as free chlorine concentration $C$, the equation may be written:

$$t = aC^b \tag{6-5}$$

$b$ is a positive number expressing the relationship between $C$ and $t$. $a$ is a constant for a given organism, water $p$H and water temperature. The slope is expressed as $-b$; then if the slope approximates $-1$, the equation may be written

$$t = aC^{-1} \tag{6-6}$$

or

$$a = Ct \tag{6-7}$$

The dotted lines in Figs. 6-11, 6-12 and 6-13 are constructed from the above equation to represent envelopes of disinfection time-chlorine concentration of various $p$H values. For example, in Fig. 6-12 the envelope $Ct = 35$ represents the envelope for the organism Coxsackie A2 at $p$H 9, and the envelope $Ct = 12$, for $p$H 7. Other envelopes for intermediate pH values are constructed by interpolation

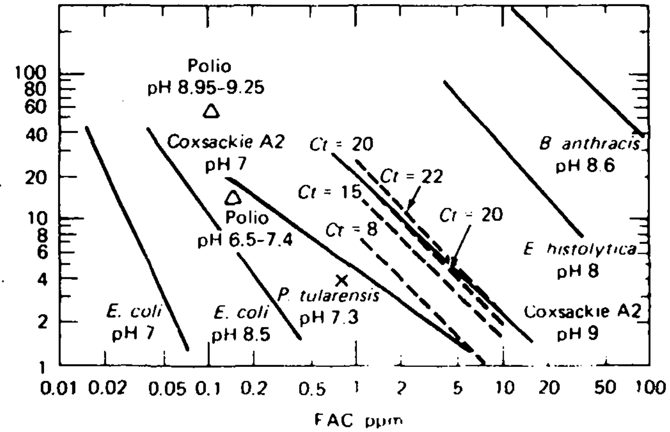

Fig 6-13 Disinfection versus free available chlorine residuals (Time scale is for 99.6 to 100 percent kill. Temperature was 10°C, with pH as indicated.) Reprinted from *Journal American Water Works Association* **54**, 1379, Nov 1962, by permission of the Association

This is based upon the HOCl concentration available from the total titrable chlorine at a given $pH$.

From all of the data shown in Figs. 6-11, 6-12, and 6-13 the question now becomes, how much chlorine should be applied and for how long should the residence (contact) time be Baumann has suggested that the minimum dose be sufficient to inactivate Coxsackie A2 virus in the treatment of small water supplies. If this reasoning is applicable to small water supplies, it should be extended to all water supplies simply to encourage better disinfection practices and provide a wider margin of safety.

Baumann[175,183] selects Coxsackie A2 virus as the indicator organism: if it is destroyed by chlorination, then all other pathogenic bacteria and viruses would also be killed. This would not include *Entamoeba histolytica, B. anthracis, Giardia lamblia,* or possibly Hepatitis A Table 6-4 gives the required values for the values of $a$ in $Ct = a$. These are shown as the dotted lines in Figs. 6-11 and 6-12.

Application of this information is most useful for small supplies that suffer from the problem of short contact time.

> EXAMPLE: A well supply with a $pH$ of 8.2 and a possible minimum temperature of 10°C shows $Ct$ 22. The well pump discharges to a pressure tank and thence to a small distribution system, so that the estimated contact time when the pump is on is six minutes
>
> Therefore $C = 22/6 = 3.7$ mg/l free available chlorine residual (not dosage). This would call for dechlorination. For a small supply, such as bus stops, trailer courts, camp sites, motels, the activated carbon pressure filter would be the preferred choice as a method of dechlorination. However, there is an alternative: A holding tank could be placed just downstream of the pump and pressure tank to provide a minimum of twenty minutes contact time. This then would require a free chlorine residual of only $22/20 = 1.1$ mg/l which would not require dechlorination.

Larger supplies, such as municipally operated systems, usually have considerably greater contact time; however, the envelopes are just as valid for large municipal

Table 6-4 Disinfection Time–Chlorine Concentration Envelopes for 0–5°C and 10°C

| | *Value of* a *in* Ct = a | |
|---|---|---|
| *Water pH Range* | *0–5°C* | *10°C* |
| 7.0–7.5 | 12 | 8 |
| 7.5–8.0 | 20 | 15 |
| 8.0–8.5 | 30 | 20 |
| 8.5–9.0 | 35 | 22 |

supplies as they are for small supplies. Part of the reasoning behind higher doses of chlorine for small supplies is that proper supervision and laboratory control are not usually available; the systems are usually designed without any alternative to long enough contact time, and are not under strict public health supervision. Most treatment plants have from one and one-half to three hours contact time from influent to treated water storage at average flows, so that the contact time for disinfection is usually easy to achieve.

Whether or not Coxsackie virus A2 could be considered the consensus organism is of course debatable. However, the idea is appealing, since it embodies all the elements of a positive and thorough approach to disinfection. In the free residual process it would be most helpful in cases of THM control to know precisely the chlorine concentration–contact time envelope to achieve the desired disinfection before the addition of ammonia and how much if any dechlorination might be required. However, so long as the health agencies and the EPA are satisfied with the total coliform concentration as proof of disinfection there will be no need to develop a consensus organism.

**Chlorine–Ammonia Process.** This disinfection process has not received much research attention since the 1940s. Most of the kinetic investigations of chloramines have been with naturally ammoniated wastewater effluents.

The kinetics of this disinfection process need some serious study now that it appears to be one of the most desirable methods of controlling THMs. Any kinetic study should include the following variables: effect of *p*H, effect of water temperature, stability in sunlight and the germicidal efficiency over a reasonably broad spectrum of conditions. The germicidal efficiency should be measured for a wide range of organisms including, but not limited to, enteric viruses, amoebic cysts, *Giardia*, hepatitis, and enteric bacteria. The objective of the germicidal efficiency investigation would be to provide a chlorine residual concentration–contact time envelope for several different organisms similar to the information provided by Baumann described above.

There are three other areas that need careful study: (1) evaluate germicidal efficiency for a variety of chlorine to ammonia-N ratios; (2) compare tastes and odors for these different ratios; and (3) compare areas 1 and 2, applying ammonia first vs. chlorine first allowing 10 min contact with chlorine before ammonia addition.

## Taste and Odor Control

**Introduction.** The term "taste and odor" should more logically be replaced by the term "flavor" as applied to the palatibility of water or for that matter anything that is ingested by humans whether food or drink. Taste itself is a sensation caused by buds on the tongue and limited to acid, bitter, salt, and sweet. All other sensations of "taste" are either combinations or are modified by smell. An additional sensation which the tongue can detect is feel or touch—slick or oily as well as metallic, dry, or astringent "Flavor" could be used as an all-inclusive term.

The origins of taste and odors in water supply are of two categories: natural and man-made. Natural sources include: aquatic growth, such as algae and diatoms and other organic compounds from decaying vegetative matter, and inorganic compounds, such as hydrogen sulfide, sulfates, and other sulfurous compounds.

Man-made sources of taste and odor in water supplies are industrial and domestic waste discharges. The worst are the discharges from manufacturing plants that contain phenols, cresols, certain amines, and mercaptans. Pulp and paper mills that discharge sulfites also cause serious taste and odor problems. With the possible exception of hydrogen sulfide, the worst offenders by far are the organic substances.

Substances causing odor are volatile and usually liquids. Most odorous substances are soluble in both water and organic liquids. Only a very few inorganic substances have odor, but they do provide the nutrients to promote the growth of odor-producing algae.

The first step in attacking a taste and odor problem is to review the literature. Several hundred articles have been published in various journals dealing with tastes and odors in the past thirty years. To save time, the serious student, researcher or operator should first read a 1977 review by S. D. Lin[186] and another by E. J. Middlebrooks in 1965.[187] These two reviews are replete with references. Another valuable reference is the AWWA handbook of specific experiences of taste and odor control in the U.S. and Canada.[188]

The next step is to learn about the Threshold Odor Test detailed in *Standard Methods*. This reference and papers by Gerstein[189] and Sigworth[190] describe in detail some of the ways to construct continuous and batch type odor monitoring devices.

There are three ways to deal with odorous contaminants: keep them out of the water, remove them from the water, or destroy them in the water. The tastes and odors produced by algae have been generally described as aromatic, fishy, grassy, earthy, musty, septic. Threshold odors caused by algae may be in some areas as low as 1–14, but in other areas go up to 30–40 and occasionally as high as 90 or more. Algal odor is generally objectionable, even when the threshold number is low. For satisfactory results the threshold odor should be reduced to 5 or less.[191]

Identification and quantitative analysis of the offending organism are important facets of taste and odor control, since the number of standard areal units per ml varies with the particular species of alga. For example, for *Asterionella* it may be 3000; for *Synura*, 200;[191] and for Dinobryon, 30.[192]

**Principal Odor-Producing Algae.** *Synura* is a very potent odor producer. A comparatively few colonies per ml will cause a perceptible odor resembling ripe cucumber or muskmelon. It can also produce a bitter taste leaving a persistent dry, metallic sensation on the tongue. When present in large numbers, it may cause a fishy odor.

*Dinobryon* imparts a prominent fishy odor when the standard areal count reaches 30 per ml. This organism develops in the southern end of Lake Michigan in June and July of almost every year.

*Asterionella* (500 units or more) imparts an aromatic geranium-like odor that changes to fishy when present in large numbers.

*Tabellaria* has a similar effect.

*Synedra* produces an earthy to musty odor, and also inhibits proper floc formation.

*Stephanodiscus* contributes a vegetable oily taste but produces very little odor.

*Ceratium* is an armored flagellate that is abundant in California and is responsible for odors varying from fishy to septic. It is likely to proliferate rapidly during any season.

*Anabena, Anacystis* (formerly known as *Microcystis, Polycystis,* and *Clathrocystis*), and *Aphanizomenon* are blue-green algae well known for developing very foul "pigpen" odors in water. In small concentrations these three algae impart a grassy to moldy odor to the water. They may in large enough masses cause luxuriant blooms. The foul odor undoubtedly develops from products of decomposition as the algae begin to die off in large numbers.

Green algae are less often associated with tastes and odors in water. Their growth may help to somewhat inhibit or keep in check the blue-green algae and the diatoms, and thereby be helpful in the control of water quality.

*Dictyosphaerium,* one of the worst offenders among the green algae, will produce a grassy to nasturtium odor as well as a fishy odor in larger concentrations. Some of the swimming green algae, such as *Volvox,* may also produce fishy odors.

Jenkins et al.[193] have reported several odorous organic sulfur-containing compounds produced in decaying blue-green algae cultures and reservoir waters containing blue-green algal blooms. These compounds included methyl mercaptan, dimethyl sulfide, isobutyl mercaptan, and N-butyl mercaptan.

*Actinomycetes* is an order of filamentous, branching bacteria. It was formerly identified with the general grouping of blue-green algae now called cyanobacteria, and encompasses several families of bacteria.[26] This group of organisms has long been suspected as the source of earthy odors in water supplies, and therefore has been subjected to intensive investigation.[194-197] These earthy-musty T/O compounds are considered to be the major source of consumer complaints.

Appreciable progress has been made in evaluating the relationship between volatile products of actinomycetes and the musty-earthy odor problems affecting water supplies across the nation. Modern research techniques have led to isolating two major earthy-musty smelling compounds: geosmin and 2-methylisoborrieol (MIB). They are metabolites of actinomycetes and blue-green algae (cyanobacteria) and show very low threshold odor concentrations.[198-200] Work done by Dougherty and Morris[201] in 1961 on the Cedar River identified the causative agent, which they called mucidone. They classified this compound as a metabolite of actinomycetes, so it was probably geosmin. Their work using chlorine and activated carbon indicated what others have found, that oxidation by chlorine is relatively ineffective but that activated carbon adsorption (granulated), to be effective (lower the threshold number to an acceptable level), requires a 25 mg/l dose. They also concluded that to be effective an oxidant would have to be able to break the carbon–carbon double bond of the T/O compound produced by actinomycetes.

Others who have attempted to control or remove the taste and odor from actinomycetes have had moderate success with combinations of activated carbon and potassium permanganate.[188] Silvey et al.[194] reported in 1950 that activated carbon and chlorine dioxide were somewhat effective but that ozone, bromine, and oxygen were not The Metropolitan Water District of Southern California had no success in removing geosmin or MIB by air stripping.[197] The realization that both oxidation and adsorption are only marginally effective in controlling the T/O compounds of actinomycetes began to focus attention on preventing proliferation of actinomycetes. This, however, is a formidable task, since these organisms are ubiquitous in the environment. They are widely distributed in terrestrial, freshwater, and marine habitats. Moreover, the terrestrial organisms have easy access to surface waters during runoff conditions. The control of actinomycetes taste-and-odor-producing compounds remains in doubt. The Metropolitan Water District of Southern California has had some success controlling the blooms of these organisms that occur in the bottom of the reservoirs. They have designed and built a mobile chlorination system using a long snakelike chlorine solution line and diffuser that can reach into all areas of these reservoirs.

**Man-made Sources of Taste and Odor.** In the following text, certain values will be given for various organic compounds as threshold taste and odor concentrations. This means that the values given are the minimum amounts that will produce a response to the taste and odor detection system of the observer—the consumer complaint level of response.

Table 6-5 gives the threshold concentration of various chemicals that produce objectionable tastes and odors in water supplies.[202] The tastes are variously described as phenolic, iodoform, medicinal, and so on.

The potentially worst offenders for taste and odor production are the discharges from the manufacture of chemicals, dyes, medicinal products, coke (quench water), ammonia recovery, wood oil, phenols, cresols, petroleum products, textiles, and paper products. Of all the various chemicals that are contributory to off flavor in potable water, the ones that have received the most attention are the phenols. This was a result of the intensification of the natural tastes of such chemicals by marginal chlorination in the early years of its use. Table 6-5 illustrates how micro quantities of certain chemicals can produce objectionable tastes and odors in water supplies. Almost from the very beginning of chlorination practice, the supplies for Chicago, Cleveland, and Toronto, among others, have been plagued with off

## Table 6-5 Chemicals that Produce Tastes and Odors

| | *Threshold Odor Level (ppm)* | |
|---|---|---|
| *Chemical* | *Av.* | *Range* |
| Acetic acid | 24.4 | 5.07–81.2 |
| Acetophenone | 0.17 | 0.0039–2.02 |
| N-amyl acetate | 0.08 | 0.0017–0.86 |
| Aniline | 70.1 | 2.0–128 |
| Benzene | 31.3 | 0.84–53.6 |
| N-Butanol | 2.5 | 0.012–25.3 |
| P-Chlorophenol | 1.24 | 0.02–20.4 |
| *o*-Cresol | 0.65 | 0.016–4.1 |
| *m*-Cresol | 0.68 | 0.016–4.0 |
| Dichloroiso propylether | 0.32 | 0.017–1.1 |
| 2,4-Dichlorophenol | 0.21 | 0.02–1.35 |
| Ethylacrylate | 0.0067 | 0.0018–0.0141 |
| 2-Mercaptoethanol | 0.64 | 0.07–1.1 |
| Methylamine | 3.33 | 0.65–5.23 |
| Methyl ethyl pyridine | 0.05 | 0.0017–0.225 |
| $\beta$-Naphthol | 1.29 | 0.01–11.4 |
| Phenol | 5.9 | 0.016–16.7 |
| Pyridine | 0.82 | 0.007–7.7 |
| Quinoline | 0.71 | 0.016–16.7 |
| Trimethylamine | 1.7 | 0.04–5.17 |
| N-Butyl mercaptan | 0.006 | 0.001–0.06 |

flavor from these chemicals. These problems were studied, evaluated, and eventually corrected by the diligence and wisdom of men like Baylis and Vaughn at Chicago, Ellms and Braidech at Cleveland, Howard and Thompson at Toronto, and Vaughn and Besozzi at Whiting and Hammond, Indiana.

It is beyond the scope of this text to include all the organic compounds that find their way into the nation's drinking water and are potential taste and odor producers, or those that are toxic when ingested. As of 1983, more than 65,000 organic compounds have been manufactured in the U.S.A. since World War II. This number increases by 3000 per year. There is great concern that the proliferation of these chemicals could devastate the nation's water supply. The U.S. EPA is concentrating its efforts to find ways that will effectively treat the volatile organics in drinking water[235]

## Role of Chlorination in Taste and Odor Control

**Algal Tastes and Odors.** Early chlorination practice consisted of the application of the absolute minimum amount to insure the maximum bacteria kill consistent with good public health practice This in most cases consisted of dosages as low as 0.25 ppm with fifteen minutes O-I residuals recorded as 0.05 ppm Compare this with current practice of dosages from 1.0 to 5.0 ppm Earlier it was also thought that the lower the dose, the lower the threshold taste from chlorination. During this time public opinion was very much against chlorination as being forced medication, and therefore the most direct and obvious mode of attack by the public was the complaint of the terrible taste it caused As a result widespread public opinion made bad-tasting water synonymous with chlorination This attitude inspired many able men in the waterworks profession to explore more vigorously the mechanics of chlorination The first assault was of course directed at improving or eliminating tastes and odors Howard of Toronto[203 205] led the way, in 1925, in exploring doses of chlorine beyond the marginal bactericidal doses. He described this approach as superchlorination At about the same time Bushnell[206] reported in 1925 that by raising marginal doses to 3 to 5 ppm, described as overchlorination, eliminated foul odors thought to be caused by gnats breeding inside a covered reservoir Griffin[121] pursued the exploration of superdoses of chlorine (up to 25 to 30 ppm) in a wide variety of conditions and practically revolutionized chlorination practice Not only did his work lead to the discovery of the breakpoint phenomenon, but it proved that the free chlorine residual fraction was not necessarily in itself a producer of off flavor. In those cases where it was demonstrated that the residual in the finished water was too great or seemed offensive, the situation was usually corrected by dechlorination. The success of heavy doses of chlorine in the raw water for the correction and control of tastes and odors that presumably originated in algae growths and/or seasonal reservoir situations is well documented.[207 211] It is evident from this information that offensive tastes from algae blooms caused by *Synura, Synedra, Dinobryon, Asterionella, Anabena, Ceratium,* and *Anacystis* can be controlled by proper prechlorination that will produce a sizable free chlorine residual—1 to 5 ppm. Taste and odor problems are not necessarily caused entirely by either odor-producing algae or trade wastes but usually by a combination that manifests itself in a continuing degradation of raw water quality While it is desirable to control the plankton count in storage reservoirs before it reaches the treatment plant, Riddick[211] has pointed out that there are so many contributing factors of geology and terrain that prevent such control that proper facilities at the treatment plant are the best assurance of taste and odor control. This would include a chlorination facility capable of carrying a free residual through the entire treatment process.

**Industrial Wastes.** Heavy doses of chlorine were first used by Howard[203] not to correct only off flavors caused by algae but primarily those caused by trade wastes. It was apparent that the worst offenders were the phenolic compounds that had their source in the wastes from coke and natural gas manufacturing plants. The addition of low dosages of chlorine to a water bearing phenols will produce a chlorophenol compound that imparts an extremely objectionable medicinal taste to the water. The reaction between chlorine and phenolic compounds has been thoroughly investigated.[212-215]

Ettinger and Ruchhoft[213] demonstrated that the result of chlorinating phenols was a reaction by steps whereby the taste-producing intensity was enormously increased by partial chlorination until a maximum intensity was reached, after which the further addition of chlorine resulted in a progressive decrease of the taste intensity until the chlorophenol tastes disappeared completely. These phenolic materials include cresol, naphthol, and dichlorophenol. In a later investigation, using more sophisticated research tools, such as gas chromatography, Burttschell et al.[214] discovered that the phenolic compound that was always present when there was a chlorophenolic taste was identified as 2,6-dichlorophenol.

It was further discovered in these investigations that, in order to eliminate tastes from these industrial wastes, the system would have to achieve a truly stable free chlorine residual and be allowed sufficient time for the reaction to go to completion. This means that time and *p*H environment are influencing factors. Ammonia in the raw water definitely slows down the reaction, but this can be overcome by increasing the chlorine dosage. As in all chemical reactions, water temperature is also a factor. The system behaves much differently in the winter months than it does in the summer months. The colder the water, the longer the contact time and the more chlorine required.

Others have demonstrated also that there is a definite ratio between chlorine required and phenolic-like substances present. However, each different water to be treated must be considered unique, and the problem has to be evaluated on an individual basis for dosage, time of contact, and so on. It has to be concluded, however, that the application of chlorine can definitely be used to destroy off flavors caused by phenolic compounds because of the many successes reported in the literature.[205,216-218][*] However, the subject of taste and odor control has become so complex, owing to the general deterioration of potable water supplies throughout the United States and Canada, that there is no single solution to the problem. Heavy doses of chlorine with plenty of contact time is not a cure-all. Supplies that have a history of taste complaints are generally equipped to combine chlorine with some form of activated carbon treatment. For example, the city of Chicago, at its South Water filtration plant, is able to apply either chlorine or activated carbon to the raw water tunnel about 1100 feet ahead of coagulation. When trade wastes produce a threshold odor value of 10 or more, carbon is added at this point; however, when the *Dinobryon* count reaches 3000 or more per ml, chlorine is usually applied here. The reason for this flexibility is that sometimes it is more desirable to apply carbon first and sometimes chlorine. Depending on the trade waste, particularly if it is predominantly phenols, it may be more economical to let the carbon do the work of absorbing the phenols to prevent chlorophenol tastes than it will be to destroy the phenols with heavy doses of chlorine and

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[*] Also see Chapter 12 the use of Chlorine dioxide as a specific treatment for the destruction of phenols

use the carbon for the absorption of the off flavors resulting from chlorination. It must be remembered that if phenols are only partially chlorinated to produce chlorophenols, very high doses of activated carbon are required to absorb the resulting chlorophenols.

Several added benefits have been discovered in the application of heavy doses of chlorine to raw water This type of treatment controls algae growth that tend to clog filter media and inhibit flocculation. Residual chlorine in the sedimentation basins prevents septicity in the sludge blanket. Therefore the maintenance of a free chlorine residual in these areas improved sedimentation and filtration. Another effect was color reduction in some waters caused by chlorine bleaching the organic matter, giving the treated water a polished look.

There is no definite upper limit on the chlorine dosages required. Usually the range is from 5 to 10 mg/l with a few instances requiring as high as 25 to 30 mg/l the record is 120 mg/l at Ottumwa, Iowa.[219,220] It is interesting to note that the successful users of heavy prechlorination doses for taste and odor control had to rely on dechlorination facilities, and those who failed either did not have enough chlorination capacity to achieve high enough doses or were not equipped to dechlorinate and therefore chose not to release water to the consumers with an abnormally high chlorine residual.

**Use of Carbon with Chlorine.** Another lesson learned in those cases where heavy prechlorination doses were used was that the consumption of powdered activated carbon was reduced significantly. Also, the application of carbon following prechlorination did not interfere with either process. Hence off flavors caused by chloro products were eliminated by the carbon while the consumption of chlorine by the carbon amounted to only about one pound of chlorine for twenty pounds of carbon applied. When phenolic wastes are known to be in the water, it takes heavier doses of carbon to absorb the chlorophenols than it does to absorb the raw phenol wastes The use of carbon or chlorine first is a question of economics: Should the phenols be destroyed by chlorine, or should they be absorbed first by the carbon?

**Seeking the Solution to a Taste and Odor Problem.** The way to success in dealing with taste and odor problems is anticipation, by considering local conditions. Some waters at certain times of the year cannot tolerate any combination of chlorine dosage and contact time without producing objectionable tastes and odors. Some of these are discussed in the chlorine-ammonia process. Knowledge of raw water quality such as threshold odor, organic nitrogen, ammonia nitrogen, degree of pollution, concentrated chloroform extract, *p*H, and temperature—is of great importance. The threshold odor data are the most important, there being no substitute for this information.

The mechanism provided by a chlorination facility to control taste and odors is to remove taste- and odor-causing substances by oxidizing them to odorless and tasteless compounds; and to control or prevent the growth of odor-producing algae and microorganisms during the treatment process and in the distribution system.

The following course of action is recommended when the T/O problem occurs in the treated water before it enters the distribution system.

Experiment first in the laboratory, because if it won't work in the lab it won't work in the plant.

*Chlorine Dosage.* Run a series of chlorine demand curves for contact times of 5, 15, 30, 45, and 60 min with a dose of chlorine normally used. If the curves plotted from the residuals at this time indicates a possible breakpoint, run some intermediate contact times to locate the breakpoint. Check the T/O for the original dose and compare to other dosages, higher and lower than the normal dose

*Ammonia.** If the problem still persists, try adding ammonia (before chlorine) in dosages to correspond to Cl:N ratios of 3, 4, 5, 6, 7, 10, and 12 to 1 Pick two contact times: 30 and 60 min. Check the residuals at these times and compare the T/O with a control sample.

*Activated Carbon and Potassium Permanganate.* If the combination of free chlorine and chloramines fails to achieve the desired results, try some combinations of chlorine and activated carbon (before and after chlorination). Also try some combinations with potassium permanganate. In addition to these combinations it will be necessary to try a variety of dosages. The combination might seem awesome, so it is always prudent to get some advice from the chemical suppliers for carbon and potassium permanganate.

**Chlorination System Requirements for Taste and Odor Control.** In order to provide the maximum choice and flexibility of control by the operator, a chlorination facility must include the following: (1) chlorination equipment adequate to produce a sufficient free chlorine residual throughout the treatment process; (2) separate automated equipment for each point of application of prechlorination, to avoid the so-called split-feed of the chlorine solution from one chlorinator; (3) automated dechlorination facilities based on residual control; (4) provision for possible preammoniation application. (5) automated postchlorination and postammoniation if distribution system residuals are required; (6) alternate points of application for activated carbon and chlorine—carbon first followed by a detention period of twenty to forty-five minutes and then chlorine for those special cases where hydrocarbon wastes are a predominate factor; (7) for taste and odor control, a minimum contact time of at least one or two hours if any ammonia is present—longer if the organic nitrogen concentration is significant—0.3 to 0.5 mg/l; (8)

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* If ammonia is used to induce a breakpoint use a Cl:N ratio of 12 1 or greater

provisions for adequate chlorine dosage and sufficient contact time prior to the raising of the pH for waters that undergo softening at high pH values (10 to 11); (9) provision for application of chlorine dioxide when indicated; (10) provision for the application of both activated carbon and potassium permanganate to the raw water if filtration is part of the process (potassium permanganate should not be used unless it is followed by filtration); (11) a continuous taste- and odor-monitoring system in a special "odor-free" room. Since taste and odor problems do not necessarily end at the treatment plant, just as much consideration must be given to the off flavors that may develop in the distribution system. It is practically axiomatic that, in systems with a tendency to develop off flavors, these unpalatable flavors will develop as soon as the available chlorine residual disappears in the distribution system. Tastes and odors from the application of chlorine are not likely to occur from the chlorine compounds themselves up to the limits listed below:

| | |
|---|---|
| Free chlorine ($HOCl$) | 20.0 mg/l |
| Monochloramine ($NH_2Cl$) | 5.0 mg/l |
| Dichloramine ($NHCl_2$) | 0.8 mg/l |
| Nitrogen trichloride ($NCl_3$) | 0.02 mg/l |

Nitrogen trichloride can cause a severe odor problem because its solubility in water is negligible. It is difficult to capture and measure in a sample as it will aerate with the slightest bit of agitation. However there is no mistaking the presence of $NCl_3$. In concentrations too low to get a response from the olfactory system it will cause the eyes to tear quite profusely. The odor of $NCl_3$ is entirely different from those of free chlorine and the other chloramines. It does not require much energy to aerate large quantities of $NCl_3$. It can, however, become an air pollution problem.

Williams[114,221,222] has demonstrated over a period of 20 years that if the ratio of monochloramine to dichloramine is kept at or greater than 2:1, objectionable tastes due to dichloramine will be at a minimum. This ratio of chloramines to achieve palatability is site-specific. It is not a hard and fast rule.

Studies by Ryckman and Grigoropolous[215] and Erdei[195] indicate the necessity for the removal of ammonia, organic nitrogen, phenolic compounds, and other organic extracts, all of which interfere with the chlorination process, with the result that it is becoming virtually impossible to provide palatable water in cases where these compounds are present in significant concentrations. These compounds are abundant in man-made wastes and should be prevented from reaching the potable water supplies. This is an impossible task; however, every effort should be made to minimize their entry into these supplies. The proliferation of toxic wastes threatening our nation's water supplies is awesome. Since World War II, 64,000 new organic compounds have been manufactured, and this number increases by about 3,000 per year. It is inevitable that these compounds will reach our water supplies, either into the ground or into the rivers and streams. The consequences can be devastating.

## Distribution Systems and Transmission Lines

**General Discussion.** The problem of delivering a palatable and safe water to the consumer does not end as the water leaves the treatment plant, pumping station, or well discharge. The difficulties of maintaining water quality in transmission conduits and distribution systems are legion. The problems of water quality control in distribution systems are of two kinds. Probably the most prevalent is that of taste, odor, and dirty water complaints. The other is deterioration of bacteriological quality.

The question of the proper solution to these problems is one of the most controversial subjects of modern water treatment practice.

There seem to be more proponents of free residual chlorine as the proper treatment than those favoring chloramine residuals. Then there are those who favor either ammonia-induced breakpoint or ammonia-controlled free residual chlorination as well as those who favor chlorine dioxide. Now that THM formation is an important consideration there will be increasing numbers of proponents favoring chloramines. It should be emphasized, however, that it is imperative in a chloramine application to maintain a residual throughout the system and to enforce a flushing program, because when the chlorine residual disappears the ammonia nitrogen returns, which is a nutrient that promotes bacterial proliferation.

**Nature of the Problem.** The deterioration of water quality in a distribution system is usually attributed to three phenomena: (1) biofouling, due to the proliferation of microorganisms, which cause tastes, odors, and dirty water, with loss of carrying capacity of the pipes and sometimes severe corrosion, (2) chemical and electrolytic corrosion, resulting in undesirable end products, such as metallic and brackish tastes as well as failure of hot water heaters and residence water piping; (3) appearance of coliform organisms in the distribution system, indicating recontamination of an otherwise safe water.

Each of these phenomena contributes to consumer complaints. The most difficult problem to handle is the proliferation of microorganisms.

Photographic evidence that a large and diverse microbe community can adhere to and colonize the interior walls of underground water distribution mains and the surfaces of suspended particulate matter in drinking water systems has been provided by Ridgway and Olson[236] and Ridgway, Means, and Olson[237] using a scanning electron microscope. Such microbial colonization can apparently take place in summer months in spite of intermittent low-level free chlorine residuals (0.1-0.2 mg/l). There is ample evidence that microorganisms attached to pipe walls or present in partially anaerobic sediments in the invert of the pipe in low-flow and dead-end portions of the distribution system are responsible for taste, odor, and color problems of potable water systems.

Proliferation of bacterial colonies on pipe surfaces and suspended particulate matter leads to a type of biofouling that can harbor and encapsulate organisms such as *Klebsiella* p. and *Enterobacter cloacae.* These organisms have been isolated in distribution systems in the presence of free chlorine residuals. This phenomenon is not yet understood but it is believed to occur in older systems where slime layers of bacterial colonies are layered with particulate matter followed by an inorganic scale of silica and/or calcium, as shown in Fig. 6-14. This sequence keeps repeating itself until a sloughing process occurs which tends to keep the layering in equilibrium. It is thought that the reappearance of coliform organisms in these systems is caused by sloughing adjacent to the inlet of the sample line.

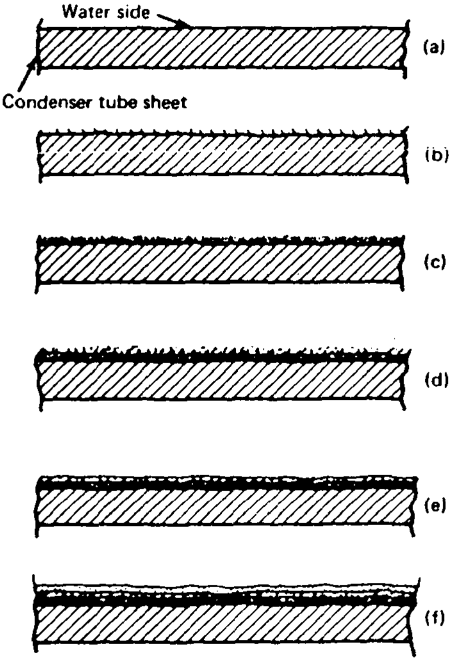

Fig 6-14 Mechanics of biofowling: (a) the pipe is new, i.e.; smooth and clean so that nothing can attach or accumulate. (b) The pipe surface becomes abraded or rough, followed by attachment of gelatinous slime forming organisms. (c) The gelatinous film serves as a microstrainer and entraps sediment. Some bacteria can promote deposition of inorganic salts as well, which sometimes is mistaken for a scale deposit. (d) Successive layers of slime and particulate matter form. (e) As time passes and if bacteria are allowed to proliferate, the mass becomes more dense. (f) It is believed that microbial colonies establish themselves in these protective layers and in time the layers spell-off discharging organisms that are well protected by this debris.

This sloughing involves the release of a piece of the top layer of the scale thereby exposing the slime layer which harbors the coliforms that are drawn into the sample line.

This notion if valid would suggest that all sampling in any distribution system should provide a representative sample of the flowing stream To determine the possibility of the type of contamination that reflects the reappearance of indicator organisms, sampling should be done at the consumer's tap Sample connections to the distribution main should extend into the pipe about one-quarter of a pipe diameter. If this is not convenient, then use a fire hydrant

The photographs taken with the electron microscope by Ridgway and Olson illustrates graphically many of the organisms discussed below They also show clearly the scale-type layer, inorganic salts, bacteria attachment material, filaments coated with debris, actinomycetes adhering to the mineral layer (scale), *Gallionella* attached to pipe surface, extracellular slime, and capsular material

**Bacteriology of Water Systems.** Bacteria are always present in water, even in the effluent from the most efficient and modern treatment plant The kinds and numbers of these bacteria are dependent upon their environments Many bacteria that may not be able to flourish in a particular environment are able to survive in a dormant state for indefinite periods of time and proliferate rapidly when the environment changes to a more favorable one The most important factor for a favorable environment is the available food supply Waters vary within wide limits as to the kind and quantities of food substances they carry, and likewise the type of bacteria which fluorish in the pipes of these systems is equally variable

Impounded surface waters that are allowed to produce abundant growths of algae and that are not filtered will contain great quantities of bacterial food in the bodies of algae that die in the pipes of the distribution system Filtration effectively removes solid foods but not the soluble ones, such as proteinaceous matter, nitrates, phosphates, sulfur, ferrous and manganous compounds, and many others.

Underground supplies seem to be the worst offenders They are low in dissolved oxygen, which contributes to anaerobic conditions, and are more likely to contain significant quantities of soluble iron and sulfur compounds, which are energy for the two most offensive species of bacteria that infest water distribution systems These are the so-called iron bacteria (*Crenothrix*, *Leptothrix*, *Clonothrix*, *Cladothrix*, and *Gallionella*) and sulfur bacteria (*Beggiatoa*, *Thiobacillus thioxidans*, and *Sphaerotilus*).

*Iron Bacteria.* The iron bacteria obtain energy by oxidizing soluble ferrous compounds to insoluble ferric compounds The amount of deposition of these insoluble compounds is large in comparison to the enclosed cells These compounds may be deposited in a sheath that surrounds the organism or is secreted so as to form stalks or ribbons attached to a cell. The iron may be obtained from the pipe itself or from the water in the system.

There are also bacteria which do not oxidize ferrous iron but may indirectly cause it to be dissolved or deposited. In their growth they either liberate iron by utilizing organic radicals to which the iron is attached or they alter environmental conditions to permit solution or deposition of iron. Less ferric hydrate may be produced, but taste, odor, and fouling may be promoted by these bacteria.

Iron bacteria are normal inhabitants of soils, and so they readily find their way into water supplies. These are never found as a single species in a pure culture. Analysis of slimes and tubercles consist of many bacteria intermingled with the crenoform filamentous iron bacteria.[223] Most of these iron bacteria can equally utilize the soluble manganese compounds, which cause black deposits as compared to the reddish brown deposits associated with iron deposition.[224,225]

The filamentous types most commonly found are *Crenothrix, Cladothrix, Clonothrix, Leptothrix*, and *Sphaerotilus*. These "crenoform" organisms cause the most serious type of biofouling if they are allowed to proliferate. These long filamentous organisms have been known to grow "massive curtains" up to two and three feet in length in concrete tunnels.

Since iron is the predominant metallic deposit they are classified as iron bacteria. These bacteria are considered a special group because their appearance closely resembles certain species of algae and fungi. There are two general types: filamentous and stalked.

These bacteria are sometimes lumped together under one general term of crenoform organisms, as they all cause equally serious biofouling.[226] This group of organisms can be differentiated by the way the branching of the filaments occur (Fig. 6-15) They utilize the manganous salts better than they do the ferrous salts, and therefore may have manganic oxide deposits on their sheaths, giving rise to black, shiny deposits. They also oxidize organic matter for energy and thus do without the metallic salts.

*Sphaerotilus* belongs to a different cultural group than the other three, but performs in similar fashion. This organism occurs abundantly in heavily polluted waters rich in organic material such as wastewaters of sugar factories and paper mills. Fig. 6-16 illustrates the sheath and cells, which occur in chains. The sheath may appear to branch, but this is recognized as false branching, as can be seen in Fig. 6-16. The cells emerging from an open end or a break in the sheath wall are called swarm cells. The hollow sheath is of organic nature, but may become encrusted with an accumulation of ferric iron deposits.[227]

The stalked bacteria, the *Gallionella* (Fig. 6-17), were formerly called *Spirophyllum* because of their twisted-ribbon appearance. It was found that this ribbon is really a stalk of almost pure colloidal iron hydroxide excreted by the small oval bacteria cell at one end. These organisms cannot utilize manganese, and their growth is depressed by the presence of soluble organic matter. They are therefore true iron bacteria in the strictest sense of the term. Another peculiarity of these

Fig 6-15 Crenothrix (200×).

organisms is that their optimum growth occurs at about 6 to 10°C; so it is often found in cold well waters or in the wintertime. In the summer months, they give way to *Crenothrix* and *Leptothrix*.

There are other members of the stalked bacteria family not usually thought of as iron bacteria, such as *Siderophacus* and *Nevskia*. The latter often contain globules of fat or sulfur, which tends to confuse the classification. The family of Siderocapsa-

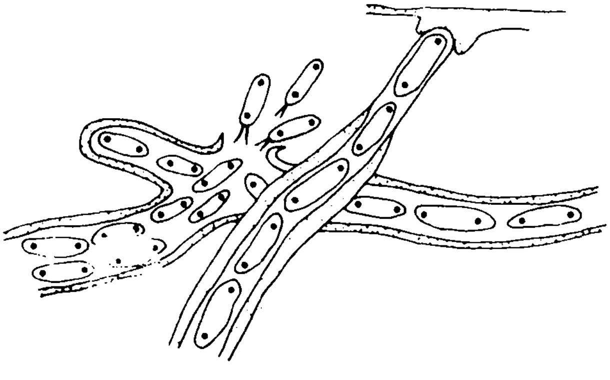

Fig 6-16 Sphaerotilus.

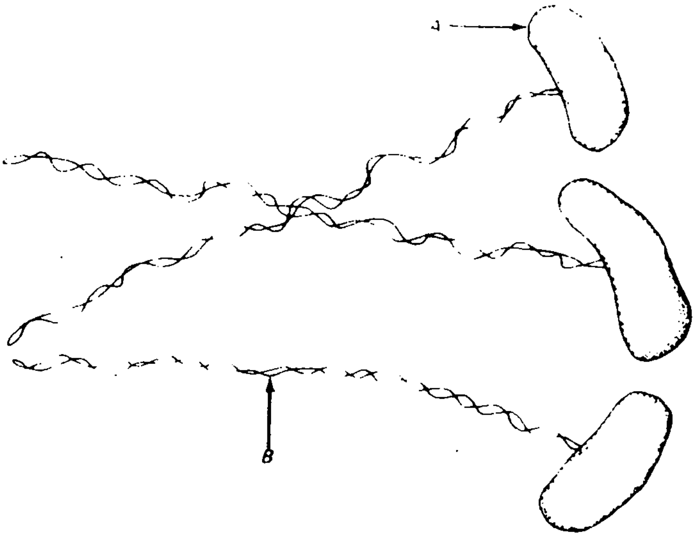

Fig 6-17 Gallionella, showing bacterial cell (A) and colloidal ferric hydroxide (B) deposited from the concave side of the cell, which form flat bands or ribbons extending from the cell. The individual ribbons twist and become entangled with other ribbons

ceae includes ten genera whose cells are usually surrounded by a thick mucilaginous capsule containing iron or manganese compounds Only one species of this group of ten genera, *Ferrobacillus ferrooxidans*, has been isolated in North America, but they are all widely distributed in European iron-bearing waters [228]

*Sulfur Bacteria* These bacteria, such as *Beggiatoa* and *Thiobacillus*, obtain the energy necessary for growth by oxidizing the sulfide ion to colloidal sulfur, which they store in their cells By metabolic action this stored sulfur is eventually oxidized to sulfates The most common of this group (*Beggiatoa*) is shown in Fig. 6-18. These organisms grow in long filaments in which can be seen granules of free sulfur and often a purple pigment They grow in a scum on the surface of sulfide bearing waters and are easily detected by microscopic examination. This filamentous group of organisms, if allowed to grow, cause serious taste and odor problems in a distribution system

Another group of sulfur bacteria that cause severe corrosion, taste, odor, and discolored water are the sulfate-splitting bacteria (*Desulfovibrio desulfuricans*) In anaerobic environments these bacteria convert sulfate and other sulfur compounds to hydrogen sulfide

Most of the bacteria which inhabit water pipes are attached forms which build colonies resembling drops of colored jelly encrusting masses varying in size from one-quarter inch up to tubercles as large as 2 inches in diameter Since these are attached forms, tap samples will not reveal the magnitude of growth inside the

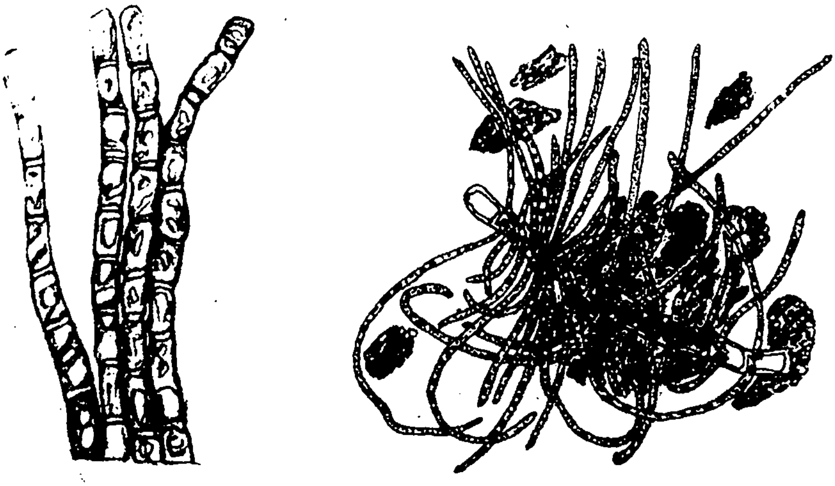

Fig 6-18 Beggiatoa (2000×) and trichomes attached to algal slime (400×).

pipes. For this reason every water distribution system should maintain accessible for routine inspection pieces of pipe in different locations that can be easily removed so that the inside of the pipe may be examined for these attached growths.

It is well known that bacteria growing inside water pipes can cause severe corrosion.[223,229,231] Thomas[232] described how water lines at a steel plant had a life of only a few months. An investigation revealed this corrosion was due to the sulfate splitting bacteria that flourished in the distribution system. This was corrected by chlorination. The action is explained as follows.[231]

The sulfate reducing bacteria splits the $SO_4^-$ ion to form hydrogen sulfide. The hydrogen sulfide either reacts with iron to form ferric sulfide or escapes through the porous ferric hydroxide scale and is oxidized into sulfuric acid by the sulfur bacteria (*Beggiatoa*). This proceeds according to the following equations:

$$SO_4^- + 10H^+ \xrightarrow{\text{sulfate-reducing bacteria}} H_2S + 4H_2O + \text{energy} \qquad (6\text{-}8)$$

and

$$2H_2S + O_2 \xrightarrow{\text{sulfur bacteria}} 2S + 2H_2O \qquad (6\text{-}9)$$

$$2S + 3O_2 + 2H_2O \xrightarrow{\text{sulfur bacteria}} 2H_2SO_4 \qquad (6\text{-}10)$$

When a tubercle is formed, the sulfuric acid is found between the tubercle and the metallic surface of the pipe enclosed by the tubercle. This explains why all such tubercles show evidence of pitting underneath them.

Iron bacteria also form tubercles, and cause both anaerobic conditions within the tubercle and low $pH$ conditions, so that the cycle of this environment plus the catalytic action caused by the iron bacteria keep putting more iron into solution under the tubercle This cycle continues with the iron bacteria, which lives on the outside of the tubercle, continuing to deposit the iron going into solution from the wall of the pipe, thus enlarging the tubercle.

Corrosion of iron pipe will not proceed when an equilibrium is established between the metal ion concentration in the water and the concentration of electrons in the metal. It is the bacteria that upset this equilibrium by putting more and more metal ion into solution.

*Tubercle Formation.* Figure 6-19 illustrates the formation of a tubercle. This is one of the most common phenomena of biofouling in a piping system. They seem to form in areas where pipeline velocities are low (<3 ft/sec), or when there are long periods of low velocity. All the evidence indicates that tubercles are of biologic origin,[226,232] apparently the outgrowth of a collection of fairly large colonies of crenoform organisms. These clusters of biologic deposits first start forming on the invert of the pipe. Long threads appear next in these jellylike clusters. The threads begin to acquire a sheath, which thickens by deposition of iron oxide, which the bacteria have taken out of solution from their water environment. Since the tubercles are hollow and spherical in shape, and since all tubercles show evidence of pipe wall corrosion by pitting within the tubercle, this suggests the evolution of $CO_2$, which would assist in the expansion of the sheaths to a bubblelike form. This would also help to explain the cause of pitting due to a low $pH$ environment. An alternative explanation is that the tubercles form oxygen concentration cells, which are also conducive to pitting. Sometimes these tubercles grow as large as two inches in diameter

In an attempt to determine the nature of common tubercle deposits, the literature reports iron oxides varying from 25 percent to 90 percent, with several analyses showing appreciable silica content

This type of biofouling not only promotes severe corrosion but also reduces the carrying capacity of the piping system Often these tubercles are first discovered when the pipe perforates under the tubercle (see Fig. 6-19). In some cases the tubercles will give off a pigpen odor when broken while still moist. This is a positive indication of organisms undergoing putrefaction. This explains why this type of biofouling can contribute to significant taste and odor problems.

*Other Types of Biofouling.* Slime-forming organisms can lead to biofouling in a distribution system. This ultimately leads to water quality degradation. Some are fungi (thallophytes) that do not contain chlorophyll. Consequently they must live on organic food or on energy available from inorganic compounds. They are mostly spore-forming and resist the most adverse conditions of moisture, heat, and chemical poisons. These organisms are usually found in waters that are heavily polluted with domestic wastewater

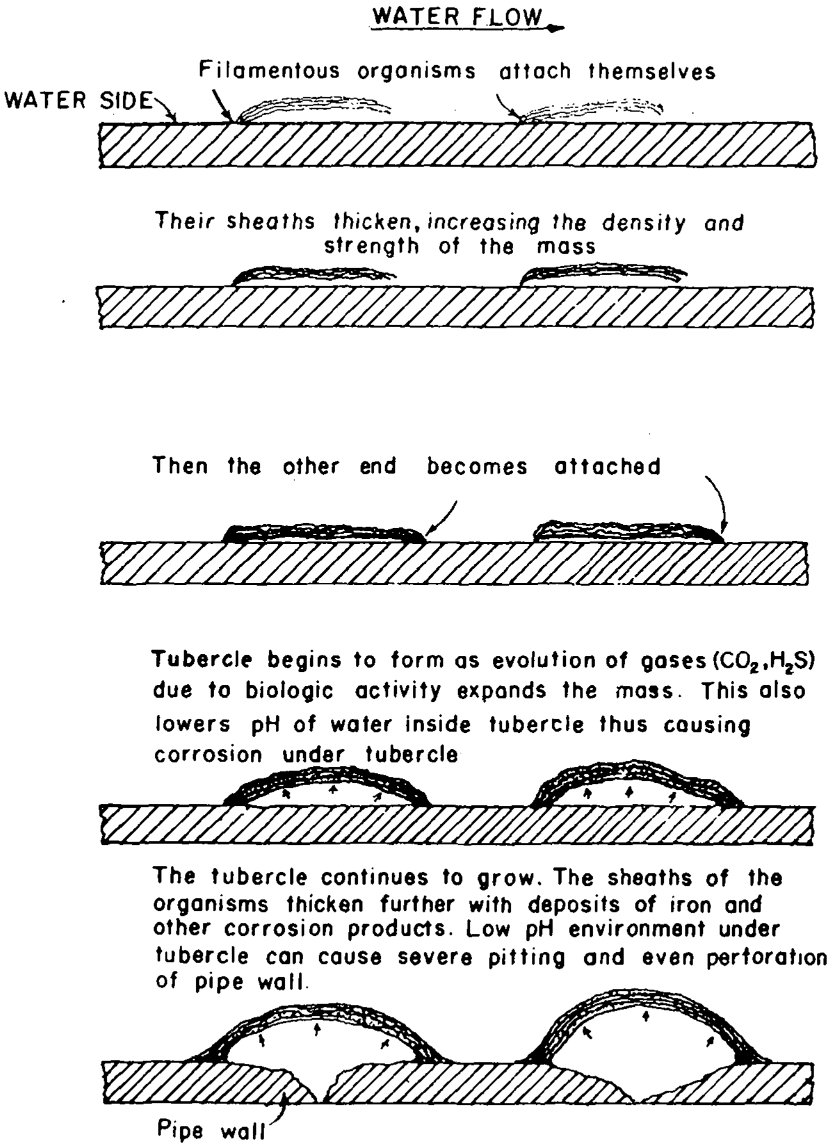

Fig 6-19 The evolution of a tubercle.

Bacteria are found in profuse quantities within the zoological slimes that lead to biofouling in a distribution system. They are unicellular plants that sometimes grow in chains or clusters. They are microscopic in size and proliferate rapidly. One organism can produce in a few hours millions of organisms in a colony. They can be classified into three structural types: the coccus, which is spherical;

the bacterium or bacillus, which is rod-shaped; and the spirillum, which is curved. Some types are aerobic, growing only in the presence of dissolved oxygen; others are anaerobic, growing in the absence of dissolved oxygen. Some are capable of producing spores; others surround themselves with a gelatinous sheath or capsule which protects them against heat, dryness, or chemical treatment for long periods.

The predominant organism found in about 50 percent of the slimes examined in the laboratory are short, gram-negative rods. The majority of these belong to the genus *Aerobacter; Aerobacter aerogenes* is the most common species (see Fig. 6-20).

Of the remaining 50 percent of the slimes studied, the predominant organisms are aerobic gram-positive, spore-bearing rods. These bacteria, when properly stained, exhibit a visible capsule. These are of the genus *Bacillus* (see Fig. 6-21). *Bacillus subtilis* and *Bacillus megatherium* have been found in many samples studied. This group develops as mucoid colonies which provide a gelatinous slime binder.

For a more detailed description of the nature, morphology, and structure of bacterial slime growths and the transformation of iron by bacteria in water, see Starkey[233] and Nason.[234]

*Coliform Regrowth.* The frequency and persistence of coliform "regrowth" in the distribution network has become a major concern to many water utilities. This continuing problem has occurred in what are considered biologically stable systems in spite of the fact that the water leaving the treatment plant is free of coliforms and cross-connections are nonexistent.

American Water Works Service Company, Haddon Heights, New Jersey reported

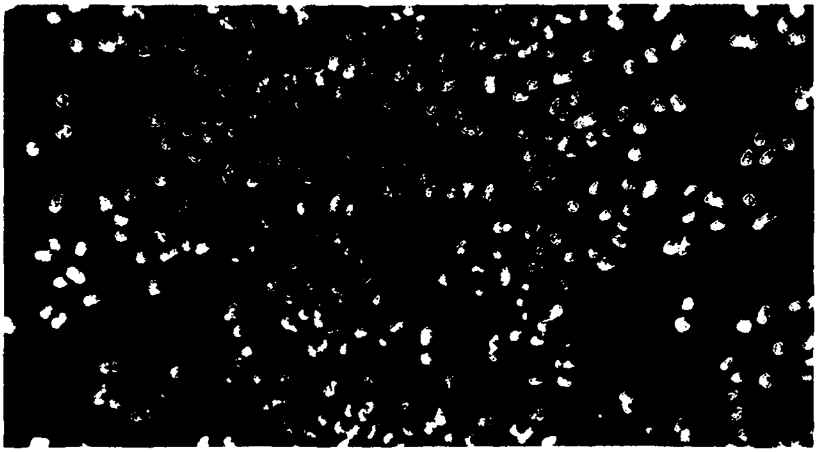

Fig 6-20 Small slime-forming capsulated coccobacilli (approximately 600×) (short gram-negative rods)

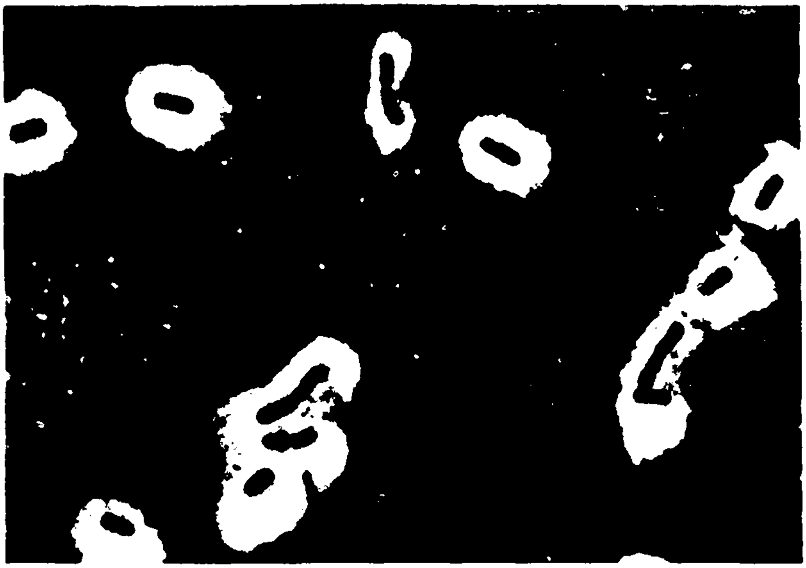

Fig 6-21 Large capsulated bacteria (approximately 550×) (gram-positive spore-forming rods).

in 1984 that six of their Midwestern water utilities had been experiencing low levels of coliforms in their distribution systems during the past four years.[312] In all cases, traditional corrective measures had failed to reduce the levels of bacteria concentration until the chlorine residual was increased to 6 mg/l These systems suffered from an unexplained appearance of coliforms in distribution systems that habitually maintained free chlorine residuals of 2-3 mg/l.[313]

In one of these systems a zinc phosphate compound was added to the treated water as it entered the distribution system. This treatment seems to have stopped the appearance of coliform organisms. Moser[313] offers the following explanation based upon his belief that the coliforms may be harbored in the gasket material at the pipe joint the zinc compound added to the water deposits a metallic film at the pipe joints, thereby encapsulating the surviving organisms. This explanation derives from the fact that the distribution system piping involved in the coliform reappearance phenomenon had been poly-pigged prior to the zinc phosphate treatment. This treatment removes tubercles and other scaly deposits that are likely to harbor or encapsulate microorganisms

Olivieri,[314] who investigated the regrowth problem that has plagued the above systems, believes the answer is the result of a microbiological process. This is the development of a biofilm by the microorganism which protects the organism from the chlorine residual He further believes that the microorganism develops this film as a consequence of the hostile environment i.e., free chlorine residual and a starvation level of nutrients White,[315] who also investigated one of these systems, thinks that age of the pipe, joint material, scaling conditions, and a system free from biofouling are all contributing factors for the survival of a sturdy strain of coliforms As one noted microbiologist said "when nutrients in the system are restricted to the poverty level as in a clean system the opportunistic organisms that do survive become street tough."

*Bacteria Enumeration.* Until recently the method for bacteria detection and enumeration (standard plate count) required a protracted length of time--sometimes days. A rapid new method was exhibited at the 1984 Annual AWWA Conference, Dallas, Texas. This is a color-guided test instrument which can perform the enumeration of as few as 100 bacteria per ml within a 2-3 minute test period.[316] This test was developed by the Baylor College of Medicine, Department of Virology and Epidemiology.[317]

Procedure and other details of this test appear on p. 918, *Standard Methods*, 16th ed. This rapid procedure will greatly simplify distribution system quality monitoring.

**Control of Biofouling in Distribution Systems.** The application of chlorine is imperative to control biofouling in distribution systems, whether it be regrowth of coliform organisms or the growths that cause taste, odor, dirty water, or corrosion. The controversial aspect of this treatment is how to apply it. Some strongly believe that the best method is to push a free chlorine residual to the far reaches of the distribution system. Others feel just as strongly that a combined residual that is predominantly monochloramine should be used.

*Free Chlorine vs. Combined Chlorine Residual.* The proponents of the combined available residual method cite the following:

1. The combined residual, while less potent, is more persistent and will eventually penetrate farther for a longer time.

2. If a free residual is pushed forward and the system is badly contaminated, this free residual in its travel will gradually be turned back toward the dip and then to the hump of the breakpoint curve and will eventually become all combined available residual. Further, during this process whereby the free residual is being converted to combined residual, tastes will result from the inevitable formation of nitrogen trichloride and dichloramines.

3. This eventual formation of combined residual chlorine is certain to occur in the consumer service pipes long after the distribution pipes have been cleaned.

4. The free residual method reacts much faster than the combined residual, which produces sloughing of the debris in the system caused by the biofouling process. This produces horribly dirty water and objectionable tastes and odors.

*Case Histories.* The proponents of the free residual method are usually those confronted with a serious situation that needs drastic action and are quick to admit serious consumer complaints while the system is being cleaned.

The ammonia chlorine process was used by Arnold[238] in 1936 to control the growth of filamentous bacteria by intrusion waters in the coast tunnel of the San Francisco water supply. The application of ammonia was discontinued when it was difficult to obtain during the war years, and was never resumed. Ackerman[239] describes controlling tuberculation using chloramine treatment.

Harvill et al.[95,96] used the unique method of utilizing ammonia to produce an induced breakpoint. By varying the ammonia dosage, they were able to control the magnitude of the residual at the dip. The ammonia was applied after the chlorine. This is a variation of the postammoniation technique recommended by proponents of chloramine residuals for distribution systems. This technique was used for about eight years until the system was cleaned, at which time the ammonia was discontinued.[97]

Alexander[243] reported in 1944 upon the successful use of free residual chlorination in cleaning and maintaining a distribution system free from biofouling originally caused by iron- and sulfur-related organisms. Gradually pushing through a 1.0 mg/l free residual over the entire system did not result in complaints of chlorinous tastes. However, the success described by Alexander came about after the system was thoroughly cleaned of massive tenacious films of organic slimes. This cleaning was done by isolating parts of the system and subjecting them to sterilization dosages of 50 to 100 ppm chlorine plus hydraulic and air purging of the pipe lines.

Brown[244] reported the use of free chlorine residuals as high as 1.5 mg/l to clean the Santa Rosa, California, system, but there were numerous complaints about chlorinous odors, which were apparently caused by the formation of nitrogen trichloride. Dechlorination, to limit the residuals going into the system, was tried, after the system had been cleaned, in an attempt to reduce complaints about chlorinous tastes and odors, sometimes described as a "Clorox cocktail" by the newspapers. This dechlorination did reduce these complaints, but soon the black fluffy slime returned to the taps. The use of dechlorination was discontinued in favor of a free chlorine residual in the distribution system in order to restore water quality to the consumer.

Wilson[244] reported the successful use of free residual chlorine, with 0.5 to 0.8 mg/l in the distribution system, which took three years and resulted in many consumer complaints about chlorinous tastes. After the system was pronounced clean, the chlorine residual entering the system was reduced from 2 to 1 mg/l with a noticeable reduction in the number of complaints.

Pomeroy and Montgomery[244] experimented at Torrance, California, between 1940 and 1949, by using both chlorine and ammonia and free residual chlorination. They were unable to clean the system by using chloramine residuals. After the system was rid of the putrefactive condition, free residual chlorination produced a water of excellent quality While they attributed a large part of the success of cleaning the system to chlorine treatment without ammonia, an intensification of swampy and musty odors, causing a storm of complaints, was experienced when free residual chlorination was substituted for the ammonia-chlorine treatment.

Blair[245] reported in 1954 of the use of free chlorine residuals to clean red water troubles caused by *Crenothrix* that had been plaguing the Palo Alto, California, water system.

*Implementing a Clean-up Program.* This carefully planned program at Palo Alto attempted to carry a 1.0 mg/l free chlorine residual throughout the entire distribution system. No objectionable tastes and odors were reported whenever the residual was as high as 0.4 mg/l but when it dropped to 0.2 mg/l or less, the complaints were prevalent After the entire system was cleaned satisfactorily, further complaints were traced to consumer service lines. A phenomenon reported by Wilson[246] was also reported by Blair In nearly all these instances, the objectionable taste and odor occurred in the morning after the water had stayed in the pipes overnight and all the free chlorine had been consumed. After this water and its chloro products had been discharged from the pipes, the taste and odors disappeared, only to recur when consumer use dropped off and the free chlorine residual again disappeared. The distribution system residual might often show 0.6 mg/l free chlorine residual while the consumer tap would not show even a trace of residual.

The foregoing demonstrated the effectiveness of chlorination in cleaning a distribution system suffering from biofouling organisms. The following is a summary of guidelines for carrying out a program to clean such a system.

1 These systems are usually supplied with underground waters that are more or less deficient in oxygen, so that the first step is to run a dissolved oxygen survey to identify the zones of degradation.

2. Implement a flushing program at the worst places, starting with the zones of least dissolved oxygen.

3. Try to push through the entire system a free chlorine residual of at least 1.0 mg/l

4. Enlist the aid of the local newspaper in indicating to the consumers the reasons for the program and how they can help by flushing their own service pipes.

5. Keep a continuous record of complaints.

6. Repeat the dissolved oxygen survey as necessary.

7 Utilize portable chlorine residual recorders where possible not only to record the residual variations but to identify as free residual chlorine.

8 Make spot checks of distribution system residuals versus adjacent consumer tap residuals. If these show a wide disparity, institute a special consumer service flushing program at no cost to the consumer for water used.

**Chlorine Residuals to Maintain Bacterial Quality.** The National Academy of Sciences and the National Research Council issued a joint report in 1955 and a clarification in 1959[24] advising that the establishment of a universal standard for maintaining residual chlorine in water in distribution systems is not desirable at this time, owing to the wide variations in circumstances encountered. This report, pertaining solely to military installations, acknowledges not only the desirability of chlorine residuals to maintain better bacteria control but that loss of the residual could be a warning of possible sabotage. Furthermore, this report recognizes that combined residuals can be maintained within a distribution system much more easily than can free chlorine residuals, but that the combined residuals are such relatively weak disinfectants that it is questionable whether the two types of residual (free and combined) should be considered analagous or even comparable unless the combined residuals used are from ten to twenty times the usual value of free residuals.

When the U.S. Public Health Service standards on water quality were revised in 1942, emphasis was placed on samples of water collected from the distribution system. Water leaving the treatment plant or pumping station could be well within the permissible bacteriological standards but might show considerable deterioration in the distribution system. The result was an increased effort to maintain chlorine residuals in those distribution systems confronted with this deterioration of quality.

Baylis and Kuehn[247] reported that the city of Chicago maintains chlorine residuals throughout their system of approximately 0.4 to 0.5 mg/l some free chlorine residuals and some chloramine.

Crabill[247] reported that

1. High-level chlorine residuals—0.4—maintain a better quality of water in the distribution systems than do low-level residuals—0.05.
2. The quality of the distributed water is reduced when chlorine residuals are lost.
3. When chlorine residuals are lost, supplemental chlorination will improve water quality.
4. There is a definite relation between water temperature and the persistence of chlorine residuals.

Plowman and Rademacher[248] found that the loss of combined residual chlorine was low when the water was in the 44 to 60°F range, but that during the summer, when the range was 68 to 73°F, there was a rapid loss of residual.

These conclusions indicate a real value in maintaining chlorine residuals throughout the system.

Umbehauer[247] reports that the use of 2.0 mg/l residuals in the far-flung El Paso, Texas, distribution system has been highly successful from a bacteriological standpoint with fewer than the anticipated number of consumer complaints.

The public health aspect of maintaining chlorine residuals in a distribution system for added consumer protection is becoming virtually a necessity. It is well known that a distribution system can become contaminated from cross-connections with non-potable water, or a water main and sewer line break at crossover points, thus causing outbreaks of a waterborne disease. This emphasizes the necessity for maintaining a chlorine residual in the distribution system.

Eliassen's analysis of waterborne disease outbreaks showed that the greatest number of cases among users of public water supplies resulted from contamination of the distribution system.[249] One of the largest outbreaks occurred at Newton, Kansas, with an epidemic of 3000 cases of bacillary dysentery in 1942. In 1952, the Kansas State Board of Health requested that cities using surface supplies maintain a minimum of 0.4 mg/l of free available residual chlorine at all consumer taps.[16] Later the same year, thirty cases of amoebic dysentery broke out among factory workers in South Bend, Indiana, caused by sewage contamination of the distribution system.[250] The 1952 request for distribution system residuals and the chlorination of all supplies was made into an order by the Kansas State Department of Health in 1956.

The investigation of the Cincinnati system reported by Buelow and Walton[240] concluded that the change from combined to free chlorine residual together with an increase in the residual concentration greatly reduced the average monthly coliform counts. Prior to the changeover from combined to free residual, the plant effluent was regulated to maintain 0.85 ± 0.20 mg/l total chlorine; to this 0.2 mg/l ammonia was added. When the changeover was made the chlorine residual was raised to 2.0 mg/l total, about 80 percent was free chlorine. This study emphasized what the Community Water System Survey[129] showed—that a chlorine residual must be maintained throughout the system in order to establish proof that disinfection has been achieved. Also the recurring cases of coliform appearances in the distribution system samples when none were detected in the treatment plant effluent indicate the necessity for continuous disinfection throughout the system. The data collected in the Cincinnati investigation strongly support the need to take bacteriological samples in known problem areas such as reservoirs, dead ends, and the periphery of the system. It has been suggested that chlorine residuals could in some cases be substituted for elaborate bacteriological sampling, provided of course that the residual is properly monitored.

In 1974 the committee on water quality in transmission and distribution systems outlined some basic requirements for a water entering a distribution network.[241] For example, if a water is of low quality with a high nutrient content, it should be carefully flocculated and filtered to produce a product low in aluminum and iron with a turbidity no higher than 0.2JTU. This water should be able to hold a chlorine residual fairly well if the piping system is relatively clean. The goal is to maintain a 0.2–0.3 mg/l total residual in the far reaches of the system. If the residual decays in the system, rechlorination may be necessary.

In 1973 the City of Chicago converted both the Central and South Water Filtration Plants to provide free chlorine residuals throughout the city.[162] In view of the mass of evidence in the literature and case histories of water quality improvement in distribution systems this change had been contemplated for some time. After one year of operation the records indicated that the switchover was a complete success in that there have been fewer consumer complaints, better bacteriological quality, and residuals can be maintained in remote dead-end areas with a modest amount of special flushing techniques.

Snead et al[242] made a comprehensive report in 1980 for the EPA demonstrating the benefits and the necessity of chlorine residual in distribution systems, with particular emphasis on free chlorine residuals

The foregoing case histories reflect success with free chlorine residuals But methods may have to be changed in some instances on account of potential THM formation in these systems The magnitude of THM formation increases with time in the presence of free chlorine Chlorine dioxide is an excellent disinfectant for distribution system chlorination because of its slow decay rate in the presence of most zoological slimes See Chapter 12.

*Relay Chlorination.* The availability of modern equipment to monitor and record either free or combined chlorine residuals simplifies the task of maintaining effective residuals throughout a distribution system. The Hartford-type installation, applicable to most systems, is described next.[251]

The water is rechlorinated solely by automatic residual control A chlorine analyzer provides the intelligence to control the chlorination equipment without the necessity of installing expensive flow-sensing devices in the distribution system This installation provides the means of obtaining residuals in that part of the system where the bacteriological quality of the water is substandard. This also is the part of the system where it is impossible to obtain residuals with chlorination at the treatment plant alone. This single point of rechlorination provides the means of meeting the U.S. Public Health standards. The attempt is to keep 0.8–1.2 mg/l free residual chlorine; however, owing to flow reversals, the residual deteriorates to as low as 0.3 mg/l and climbs to as high as 2.0 mg/l for a few hours each day This approach has proved successful in many instances It is particularly useful where open balancing reservoirs deplete the residual in the distribution system.

*Practical Considerations.* Careful planning of the distribution system and the proper location of balancing reservoirs can largely prevent situations that tend to cause such wide fluctuations in distribution system residuals As an example, more attention should be given to the prevention of dead ends This will require a periphery type of grid system to improve the circulation of a distribution system. The literature abounds with dead end water quality problems, but apparently the designers of such systems are totally unaware of the consequences of poor circulation

Research is also needed to properly determine whether free residual or combined residual chlorine is preferable in a distribution system As a broad general rule, it is better to have a predominantly monochloramine residual, rather than a free residual, entering a relatively clean system The chance of developing nitrogen trichloride is nil if the residual entering the system is primarily monochloramine. However, if a system is dirty, then free residual chlorine must be used to do the cleaning as soon as possible Such applications are bound to produce nitrogen trichloride and dichloramines in quantities sufficient for the consumers to complain of tastes and odors These obnoxious chlorine compounds will persist until the free chlorine residuals penetrate to all parts of the system, which is accomplished by a continuous flushing program with sufficient high free residuals to do the job

Another area that needs more attention is that of the corrosion potential of the system residual As an example, Williams[222] used a combined residual at Brantford, Ontario, to maintain proper water quality and prevent the formation of tastes and odors in the distribution system. Owing to the presence of significant concentrations of organic nitrogen (1-3 mg/l) in the raw water and the necessity of using the free residual chlorination process at the treatment plant, nitrogen trichloride was produced at the treatment plant. If free chlorine residuals were allowed to enter the distribution system, then nitrogen trichloride would develop in the distribution system, causing taste and odor complaints. To prevent the subsequent formation of nitrogen trichloride in the distribution system, postammoniation was practiced.* Sufficient ammonia was added to convert all the free chlorine residual to combined residual, and enough in excess of this to produce a combined residual consisting of 80 percent mono- and 20 percent dichloramine going to the distribution system. If the organic nitrogen content were high, the dichloramine fraction would be higher, and vice versa. The total combined residual going to the distribution system was kept between 0.6 and 0.8 mg/l.

At one time this water passing through the distribution system developed a progressively deteriorating palatability, with the resulting taste described as "bitter irony." A thorough investigation revealed a pickup of zero to 0.8 mg/l ferrous iron and a shift in the chlorine residual to 40 percent mono- and 60 percent dichloramine with the monochloramine deteriorating from about 0.6 mg/l to about 0.15 mg/l. The drop off of chlorine residual in the system was proportional to the pickup of ferrous iron. There was also a drop-off in ammonia content as high as 75 percent in two hours as the water passed through the distribution system. However, samples stored in the laboratory showed complete stability of chlorine residual and ammonia content. The difficulty was finally discovered to be aggressive water. Analysis showed that the heavy prechlorination doses combined with the addition of aluminum sulfate for turbidity removal resulted in a sufficient loss in alkalinity and a lowering of the *p*H to make the treated water aggressive. This aggressive water contained enough free $CO_2$ to attack the iron pipe, causing ferrous bicarbonate to go into solution. This resulted in the dechlorination of the monochloramine fraction producing microquantities of ferric hydroxide, which eventually flushed from the system without causing red water troubles. The stability of the dichloramine fraction of the residual is somewhat of an anomaly, but can be ex-

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* The preferred method to prevent $NCl_3$ formation and the elimination of dichloramine is complete dechlorination with $SO_2$ followed by rechlorination Williams chose postammoniation because it required less capital expenditure for equipment

plained. Williams points out that when the organic nitrogen increases, so does the dichloramine proportion of the total combined residual The high organic nitrogen content of the raw water can easily be due to pollution from sewage Since sewage contains urine and other compounds containing significant quantities of creatinine, the stable dichloramine fraction is probably a chlorcreatinine compound* that exhibits the chracteristics of dichloramine in the amperometric titration procedure. It has been found that such compounds are quite stable but with little or no germicidal power.

Williams confirms the fact that there is no off flavor resulting from the dichloramine fraction. The monochloramine fraction is considerably more susceptible to dechlorination by ferrous iron than is dichloramine, and so the gradual disappearance of monochloramine residual as the water passes through the distribution system is not unexpected.

The problem of the iron pickup and the resulting "bitter irony" taste was solved at Brantford by the addition of lime to the treated water, which restored the alkalinity and raised the *p*H to normal values in accordance with Langelier's equilibrium index. Now the water has the ability to lay down a slight protective film of calcium carbonate on the metal pipes.

Various experiences, extending over many years, some of which are described in the foregoing text, show that chlorine residuals in a distribution system: control growths in the system; improve the palatability of the water; give added consumer protection against waterborne diseases; protect against accidental and possibly intentional contamination of the system.

**Restoring Pipeline Capacity.** The application of chlorine to long transmission systems is somewhat akin to the maintenance of chlorine residuals in a distribution system. The principal difference is that there are seldom any consumers supplied by the transmission system, and therefore the public health aspect and the taste and odor control problems are usually not factors. These systems usually terminate at the treatment plant. If not, then the transmission line is simply part of the distribution system. It has been demonstrated that filamentous organisms can create a condition inside pipes to significantly increase the friction loss, thereby reducing the design capacity.

Rogers[253] reported a slime deposit of ⅜ to ½ inch thick attached to the cement lining of a 42- and 48-inch transmission line thirty-four miles long. This deposit was 75 percent ferric oxide and contained *Crenothrix*. The capacity of the line dropped from 30 to 20.4 million gallons in three years. Continuous chlorination of 3 mg/l restored the capacity of the line, and, by maintaining a free residual of chlorine at 0.4 to 0.5 mg/l at the end of the line, prevented growth of the *Crenothrix* and thereby maintained the C factor in the line

Griswold[254] used chloramine treatment on a 24-inch supply line twelve miles long. After fifteen years of continuous treatment with a terminal residual of 1.0

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* We now know that the dichloramine fraction in the presence of organic N is a mixture of impotent but stable organochloramines. See Chapter 8

to 1.5 mg/l combined chlorine, the line showed an average loss of 10 percent in capacity in seven years. The line is now cleaned every five or six years, while prior to chloramine treatment the line had to be cleaned every twenty months; but, in order to achieve the nominal carrying capacity of this line on a continuous basis provided by the chloramine treatment, the line would have to be cleaned every seven months if the treatment were discontinued.

The San Diego aqueduct, which travels some seventy miles from the west portal of the San Jacinto tunnel to the San Vicente reservoir in San Diego originally had a capacity of 104 cfs. This dropped to 94 cfs, and slime growths were suspected. Streicher[255] reported on the success of intermittent chlorination of this line to maintain the original capacity of 104 cfs. After much experimentation it was found that a 2.2 mg/l chlorine dose for two hours twice a week was sufficient.

The experience at Little Rock, Arkansas, described by Jackson and Mayhan,[256] graphically illustrates how much more difficult it is to clean a transmission line after the onset of slime growths than it would be to prevent the growth from forming. A 39-inch transmission line thirty three miles long was put into operation in 1938 with a *C* factor of 147 and a carrying capacity of 25.32 mgd. In one year this line was reduced in capacity by 20 percent.

The slime deposit of black jellylike organic material varied from a thin film to a mat ¼ inch thick and was heavily interspersed with iron oxide. The dominating organisms were found to be large gram-positive encapsulated bacteria and *Crenothrix*. The water supply originated at Lake Winona, a soft water of only 15 mg/l hardness and an iron content of approximately 0.4 mg/l. Chloramine treatment was begun in 1939 at 1.25 mg/l with a residual of 0.55 mg/l (starch-iodide) at the terminus of the line, which was the influent to the treatment plant. This treatment proved to be only moderately successful in restoring the line capacity. One year later free residual chlorine treatment was begun, and after nine years of a 5 mg/l dose resulting in a 1 mg/l residual at the plant the line was considered to be almost like new. The *C* factor had risen to 133 with a 22.75 mgd capacity in 1950. At this point, since the line was considered to be relatively clean, intermittent treatment with superdoses of chlorine was substituted for continuous treatment. Doses of 12 mg/l for about 2 or 3 hours per day resulted in residuals of 8 to 10 mg/l at the plant. Dechlorination of these residuals was found to be unnecessary, as they dissipated rapidly in the large settling basins. The intermittent treatment, which consumed only about 250 pounds of chlorine per day, resulted in an annual savings of approximately fifty thousand dollars, thus demonstrating the exorbitant cost of the cure as compared to the cost of prevention.

The first step in any program designed to maintain a transmission line is to anticipate the problem of slime growths. When the line is first put into operation, the coefficient of friction should be determined while it is in the new, clean condition. This will establish an irrefutable reference point to determine when the line needs cleaning, and will provide a means for evaluating any needed chemical treatment. The friction factor should be checked each month of the first year of operation to get a slime growth profile.

The effect of corrosion and tuberculation on the friction coefficient of metal pipelines is well known. However, for many years it was thought that concrete pipe or cement-lined steel pipe would maintain their capacities indefinitely. This has proved to be an incorrect assumption, since it has been abundantly demonstrated that filamentous organisms, freshwater sponges, and other organisms are able to attach themselves in massive quantities to concrete and various types of cement surfaces. The carrying capacity of such lines drops off rapidly without any increase in roughness, simply because of the reduction in the effective diameter of the pipeline. Derby[257] cites the *C* factor of a 5-foot concrete pipe fifty miles long dropping from 140 to 95 because of massive growths of fresh-water sponges *Asteromyenia plumosa* and *Trochospongilla leidyi.*

Another unknown factor that has caused serious trouble in transmission systems is the possibility of groundwater intrusion into the concrete-lined tunnels carrying the water supply. These waters are often the source of iron and sulfur bacteria infestation. This was the cause of luxuriant growths of *Crenothrix* in the coast tunnel of the San Francisco water supply and the source of sulfur-bearing water in the Santa Barbara supply. The San Francisco coast tunnel capacity decreased 30 percent in three weeks.[238]

Control of such growths in transmission lines requires careful study to determine the proper course of action. This may be cleaning followed by chemical treatment with chlorine, chloramine, and possibly copper sulfate. It may not be possible to accomplish satisfactory cleaning. If chemical treatment is to be used without cleaning, it should be determined whether or not the line velocities are sufficient to flush out the organisms destroyed by the chemical treatment. For long conduits of varying cross sections, chemical treatment may be cheaper and more satisfactory than mechanical cleaning. Intermittent chemical treatment must also be considered where taste and odor problems are not involved. If the organisms cause taste and odor, some program of continuous treatment will probably be necessary to prevent these growths from forming. Open channels are subject to sunlight, which has the ability to destroy free chlorine residuals. Therefore these situations call for some kind of variation of the chemical treatment—possibly a combination of chloramine and copper sulfate, intermittent or continuous. If intermittent, the treatment should be confined to the hours of darkness if it is found that free residual chlorine is most effective.

## Aid to Coagulation

Prechlorination to free residual is nearly always effective in improving coagulation or reducing the coagulant dose or both. This phenomenon has been known for some time.[258,259] It is not clearly understood how chlorine acts as a coagulant aid, although it is probably due to its oxidizing effect on organic matter.

Chlorine is also used in the preparation of the ferric ion as a coagulant for use in certain types of color and turbidity removal processes. In these instances chlorine solution from conventional chlorination equipment is added to either a solution of pickle liquor or copperas, both of which are ferrous sulfate. Chlorine converts the ferrous ion to ferric, which hydrolyzes to form ferric hydroxide, a fluffy gelatinous floc. Copperas is a granular free-flowing material easily handled in a dry chemical feeder. The chlorine is added downstream from the solution chamber outlet of the copperas feeder. These systems have special application where the optimum *p*H for coagulation is in the range of 8 to 9. It requires one part of chlorine to react with 7.8 parts copperas to convert all of the ferrous to ferric iron as follows:

$$6FeSO_4 \cdot 7H_2O + 3Cl_2 \longrightarrow 2Fe_2(SO_4)_3 + 2FeCl_3 + 7H_2O \qquad (6\text{-}11)$$

Chlorinated copperas has been known to form a tough, rapidly settling floc with as little as 0.5 grains per gallon dosage.[260]

Chlorine is also used in the preparation of activated silica, a coagulation aid.

## Aid to Filtration

At one time it was thought that the efficiency of filtration depended in part upon the establishment of a very thin film of organic material on the sand grains, and that a chlorine residual would destroy this organic film, thereby decreasing the efficiency of the filter.[261] This notion was soon discarded when it was discovered that the proliferation of microorganisms in the filter media would seriously impair the effectiveness of filtration. Baylis of Chicago insisted that *all* surface supplies should be chlorinated as soon as the water reached the treatment plant, as is recommended for polluted supplies.[262]

Baumann et al. reported in 1963 on a controlled study of prechlorination and its effect on filter efficiency.[263] They found that the prechlorinated filter operated considerably longer than the control filter which was not prechlorinated. Other observations included: prechlorination reduces the depth of suspended solids into the filter sand; less sand was removed during the cleaning process; oxidizable tastes and odors were destroyed; oxidizable organic matter was confined to the surface cake at the sand surface; the bacterial quality of the filter effluent was considerably improved as compared to the unchlorinated control filter.

An adequate free residual chlorine is necessary to maintain filter runs and to prevent the formation of mud balls, which not only impair the filtration efficiency but interfere with proper backwashing. This chlorine residual prevents organic growths that contribute to slime buildup on the filter media. These growths not only reduce the mechanical efficiency of filtration but contribute to the degradation of the bacterial quality of the filtered water.

Certain types of algae are also well known for contributing to the clogging of filters. The most serious offenders are the diatoms, which are present during all seasons of the year - *Asterionella, Fragilaria, Tabellaria,* and *Synedra.*

In Chicago, when the water to be filtered contained approximately 700 organisms per ml., principally *Tabellaria* and *Fragilaria,* the filter runs were only 4.5 hours.

Three days later, when the count was down to 100 per ml the filter runs increased to forty-one hours.[191] In Washington, D.C., filter runs were reduced from an average of fifty hours to less than one hour by the sudden influx of the diatom *Synedra,* which had a concentration in the raw water reaching 4800 cells per ml.[191]

If the filter-clogging blue-green algae—*Anacystis, Rivularia, Anabena,* and *Oscillatoria*—are allowed to grow, they form a loose slimy layer over the sand grains, thereby reducing the flow of water through the filter.

Organic growths on the sand grains or other media within the filter reduce the length of filter runs and cause the formation of mud balls, which seriously impair backwashing efficiency. These same organic growths provide an anaerobic environment, which contributes to the rise of the ammonia nitrogen content in the filter effluent. If this is not counteracted by free residual chlorination, nitrifying bacteria such as *Pseudomonas* may proliferate, causing the conversion of the available nitrogen to nitrites. At this point, with the development of nitrites, the environment becomes most suitable for the proliferation of other bacteria, thereby degrading the bacterial quality of the effluent. This situation can be prevented only by a free residual chlorine. Combined chlorine will not oxidize the nitrites to nitrates; only free chlorine (HOCl) can do this.

A filter that has become fouled by organic growths can often be restored by prechlorination. At first the only residual that will appear in the effluent will be all combined residual—meaning that it is predominantly monochloramine. This suggests the presence of significant amounts of ammonia developing within the filter media because of the organic growths. If the prechlorine dose is gradually increased, the organic material will become more and more oxidized. Within a short period of time—possibly one or two weeks—the total residual of filter effluent should begin to show a trace of free chlorine. When the free chlorine content is 80 to 85 percent of the total residual, it may be assumed that the filter is relatively free from organic growth. Backwashing will become more effective and filter runs will be considerably increased, and the bacterial quality will return to acceptable standards. The application of chlorine ahead of filters that have not been properly cared for by prechlorination will not necessarily achieve the desired results. Some filter media that have been neglected for a long time simply cannot be cleaned by adequate chlorination; these media should be discarded and replaced with new material.

Since free residual chlorination is an aid to both coagulation and filtration, it becomes patently clear that the case for carrying a free chlorine residual throughout the entire treatment process becomes strong indeed. It also indicates the necessity of a special point of application of chlorine just ahead of the filters.

## Hydrogen Sulfide Control and Removal

Hydrogen sulfide is probably the most obnoxious and troublesome compound to be dealt with in a potable water supply. It is an almost impossible task to produce a palatable water that is free of taste and odor at all times if hydrogen sulfide is present in the raw water in significant concentrations. Not only does the treatment process require continuous surveillance, but the distribution system and consumers' hot water systems require monitoring.

Hydrogen sulfide occurs mainly in well waters. Occurrence in surface supplies is primarily by groundwater intrusion; however, with the rising pollution of natural waters by sewage and industrial wastes, surface waters may become contaminated with hydrogen sulfide.

Sulfides in well water are probably produced through chemical and bacterial changes under anaerobic conditions far underground. Sulfates may be reduced to sulfides by organic matter under anaerobic conditions, and the resultant metallic sulfide changed to hydrogen sulfide by the action of carbonic acid.

The sulfate reducing bacteria (*Desulfovibrio desulfuricans*) are another source of hydrogen sulfide production. In anaerobic environments these bacteria convert sulfates and other sulfur compounds to $H_2S$. They have a growth range of pH 5.5 to 8.5 and are found to exist in temperatures of 0 to 100°C, with an optimum range of 24 to 42°C.[264]

Another group of bacteria also plays an important part in sulfur bearing waters. These are the sulfide oxidizing forms. The most prevalent are *Beggiatoa* and *Thiobacillus*. *Beggiatoa* are filamentous white sulfur bacteria that obtain the energy necessary for their growth by oxidizing the sulfide ion to colloidal sulfur, which is then stored in their cells.

Hydrogen sulfide is a flammable and extremely poisonous gas.

Brief exposures (30 minutes or less) to $H_2S$ concentrations as low as 0.1 percent by volume of air may be fatal. The gas is highly soluble in water to the extent of 4000 mg/l at 20°C and one atmosphere. The minimum detectable concentration by taste in water is given as 0.05 mg/l.[264] In aqueous solutions it hydrolyzes as follows:

$$H_2S \rightleftharpoons HS \; + H^+ \qquad (6\text{-}12)$$

The hydrosulfide ion ($HS^-$) further dissociates as follows:

$$HS^- \rightleftharpoons S^= + H^+ \qquad (6\text{-}13)$$

At 18°C the hydrolysis constant for Eq. (6-12) is:

$$K_h = 9.1 \times 10^{-8} = \frac{[H^+][HS\;]}{[H_2S]} \qquad (6\text{-}14)$$

And for Eq. (6-13)

$$K_h = 1.2 \times 10^{-15} \frac{[H^+][S^=]}{[HS^-]} \qquad (6\text{-}15)$$

Figure 6-22 illustrates the distribution of $H_2S$, $HS^-$, and $S^=$ for various pH levels. At *p*H 7, hydrogen sulfide is approximately 50 percent of the total dissolved sulfides; at *p*H 5, it is practically 100 percent of the total; at *p*H 9, it is nearly all hydrosulfide ion. Therefore the existence of hydrogen sulfide in sulfur-bearing waters is *p*H dependent. This scientific fact has been well documented.[265,268,269,274]

Whenever the equilibrium between the hydrosulfide ion and the hydrogen sulfide in solution is upset, as when $H_2S$ is removed by oxidation; the shift will be to form more $H_2S$ from the remaining dissolved sulfides to reestablish the equilibrium. This stored sulfur gradually disappears by metabolic action, being itself oxidized to sulfate to yield more energy.

The primary objection to waters containing hydrogen sulfide is the offensive rotten-egg taste and odor. The secondary objection is the marked corrosiveness of these waters to both metals and concrete structures. Another serious problem is their ability to promote luxuriant blooms of the various types of filamentous sulfur bacteria that lead to a general degradation of water quality in the system.

The presence of $H_2S$ will turn silverware black, discolor lead base paint, make bathing in tubs or showers extremely unpleasant, and stain all plumbing fixtures. The sulfides in the water react with iron from the mains to form a suspension of iron sulfide that causes a discoloration of the water. This suspension makes laundering almost impossible.

The presence of hydrogen sulfide is noticeable to the extent of 0.5 mg/l even in cold water.[265] If the pH is high, the odor may be slight. Concentrations of $H_2S$ as low as 0.2 mg/l will promote the growth of *Beggiatoa.*[264] The range of hydrogen sulfide concentration in usable sulfur waters is below 10 mg/l. Notable

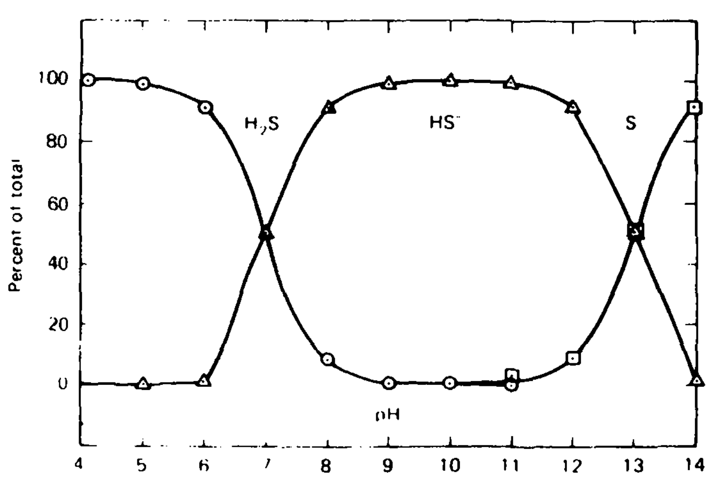

Fig 6-22 Effect of pH on hydrogen sulfide-sulfide equilibrium.

exceptions are the Wadsworth Plant of the Southern California Water Company[266] and the Santa Barbara supply[267] where the $H_2S$ content in the raw waters sometimes reaches 20 mg/l.

The chemistry of the oxidation and removal of hydrogen sulfide is extremely complex. Supposedly the oxidation proceeds to form either elemental sulfur, sulfate, or both, as follows:*

Aeration or oxidation by dissolved oxygen in the water

$$2S + 2O_2 \rightarrow SO_4 + S_1^0 \tag{6-16}$$

by chlorination

$$H_2S + Cl_2 \rightarrow 2HCl + S_1^0 \tag{6-17}$$

and

$$H_2S + 4Cl_2 + 4H_2O \rightarrow 8HCl + H_2SO_4 \tag{6-18}$$

Theoretically Eq. (6-17) requires 2.1 mg/l chlorine for each mg/l $H_2S$, and Eq. (6-18) requires 8.5 mg/l for each ppm $H_2S$. This reaction was amply demonstrated in field experiments by Powell.[274]

The assumption is that if enough chlorine is added to satisfy the natural chlorine demand of the water plus enough to react with the $H_2S$ present, then free sulfur will be formed in Eq. (6-17), and that if more chlorine is added to satisfy the stoichiometric requirements of Eq. (6-18), then all the $H_2S$ will be converted to sulfates. Unfortunately, this is not the case.

When chlorine is added, regardless of the amount, to a sulfur-bearing water, colloidal free sulfur will be formed if enough chlorine is added to more than satisfy the natural chlorine demand of the water. This formation of free sulfur is readily evident as a milky blue turbidity (the Tyndall effect).

Choppin and Faulkenberry[270] state that the oxidation of the alkali sulfides is not simple and direct and may yield as end polysulfides, sulfites, and thiosulfates in addition to elemental sulfur and sulfates. The relevancy of this statement is based upon practical evidence that most sulfur-bearing waters that have been treated for hydrogen sulfide removal will exhibit some magnitude of odor in hot water systems. While the odor is not that of hydrogen sulfide, it is a sulfurous odor. Monscvitz and Ainsworth[267] believe that this odor is the result of the formation of polysulfides ($HS_n$ ) in the oxidation reaction of hydrogen sulfide. Given time in days, these polysulfides will eventually oxidize to sulfates in the presence of dissolved oxygen in the water. If dissolved oxygen is not present, as occurs in distribution systems, these polysulfides may be reduced back to hydrogen sulfide.

The oxidation of hydrogen sulfide will produce colloidal sulfur which can be removed by filtration. Side reactions will produce polysulfides which must be

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* See Chapter 7 for more details on hydrogen sulfide chemistry.

dealt with in order to eliminate threshold odors in the finished water Monscvitz and Ainsworth suggest the conversion of colloidal sulfur and the remaining polysulfides to sulfates by first adding sulfite (which forms thiosulfate) and by converting the thiosulfate ($S_2O_3$) to sulfate by rechlorination as follows

$$\begin{array}{l} S^0 + SO_3^{=} \rightleftharpoons S_2O_3 \\ \Updownarrow \\ HS_n^- \end{array} \tag{6-19}$$

$$S_2O_3 + HOCl \longrightarrow S_4O_6^{=} + SO_4^{=} \tag{6-20}$$

The reaction of Eq. (6-19) is very rapid. The formation of tetrathionate ($S_4O_6$ ) is not significant since it will convert to sulfate within a short time, with no contribution to any threshold odor. The sulfite ion may be added as sulfur dioxide in an aqueous solution or as sodium metabisulfite. This reaction taken to completion is recognized as the typical dechlorination reaction.

Above *p*H 9.0, polysulfides do not appear to form. This is probably one reason that any lime-softened sulfur-bearing water will not produce threshold odors resulting from these compounds.

Probably the most important factor in hydrogen sulfide removal is that of contact time. Given time and an oxidizing agent, all dissolved sulfides can be converted to sulfates.

Aeration with contact times of up to three hours have shown hydrogen sulfide removals of 2 to 3 mg/l and 35 to 45 percent removal of dissolved sulfides.[271] Shorter contact times and raw water concentrations of 5 mg/l $H_2S$ reduced to 1 mg/l by aeration, followed by coagulation and filtration, require free residual chlorine of up to 0.35 mg/l for the complete removal of $H_2S$.[272] Derby[273] reported in 1928 on the satisfactory removal of up to 7 mg/l by conventional lime-softening and chlorination. Concentrations as high as 32 mg/l have been successfully removed by pre- and postchlorination, coagulation, and filtration.[266]

The final concern of the water producer is to protect the quality of the product in the distribution system This is difficult to accomplish because of the possible growth of sulfur bacteria While the oxidizing forms that grow in an aeration tower may be beneficial because of their ability to convert the sulfide ion to sulfates, they may find their way to the distribution system and in their life cycle slough off into dead ends and contribute sulfur compounds that under anaerobic conditions will start the entire hydrogen sulfide production cycle over again For this reason chlorination for the control of these organisms in the distribution system is of utmost importance

Hydrogen sulfide can be successfully removed by aeration and chlorination, followed by the addition of sulfur dioxide or sulfite for the removal of polysulfides and colloidal sulfur and then rechlorination to convert all the remaining sulfur compounds to sulfates.

The formation of hydrogen sulfide is *p*H dependent and is encouraged by a lower pH

Oxidation of sulfur-bearing waters will produce colloidal sulfur that may cause a milky blue turbidity (the Tyndall effect).

As the hydrogen sulfide is removed by oxidation, the equilibrium shifts to form more $H_2S$ from the remaining dissolved sulfides; depending upon the amount of oxidant and contact time, this reaction can continue until all the dissolved sulfides are removed

When sulfur-bearing waters are oxidized, a combination of sulfur compounds are formed, including colloidal sulfur, polysulfides sulfites, and sulfates

Aeration, chlorination, coagulation, filtration, and softening have been used successfully for the removal of $H_2S$.

Chlorination is extremely important not only as an oxidant but also as a germicide to prevent the growth of unwanted sulfur bacteria.

Complete removal of $H_2S$ can best be accomplished by oxidation by chlorine; conversion of resulting colloidal sulfur and polysulfides by metabisulfite or sulfur dioxide to thiosulfates, and then converting to sulfates by rechlorination.

## The Iron and Manganese Problem

**Nature and Occurrence.** Both iron and manganese cause serious problems in potable and industrial water systems. While it is beyond the scope of this text to cover the subject of iron and manganese removal, it is pertinent to discuss the occurrence of these elements in water supplies, their significance, and the role of chlorination as related to compounds of these substances.

These two elements are relatively abundant in the earth's crust. The lithosphere contains approximately 5 percent iron and 0.1 percent manganese.[276] Iron exists in soils and minerals, mainly as insoluble ferric oxide and manganese, as manganese dioxide. Iron also occurs as ferrous carbonate (siderite), which is slightly soluble. Since groundwaters usually contain substantial amounts of carbon dioxide (30 to 50 mg/l), appreciable amounts of ferrous carbonate may be dissolved to form soluble (150 mg/l) ferrous bicarbonate as follows:

$$FeCO_3 + CO_2 + H_2O \longrightarrow Fe(HCO_3)_2 \qquad (6\text{-}21)$$

This is the commonest form in which iron is found in water supplies in troublesome amounts. Iron in natural water supplies may also be present as ferric hydroxide, ferrous sulfate, and colloidal or organic iron.[265]

The insoluble ferric compounds will only go into solution under reducing conditions--in the absence of oxygen. The same holds true for the compounds of manganese.

Manganese most commonly occurs in water supplies as manganese bicarbonate, which is even more soluble than ferrous bicarbonate. Acid mine waters frequently contain manganous sulfate as well as ferrous sulfate; some shallow wells and surface waters contain colloidal or organic manganese

The occurrence of iron and manganese in water supplies is usually limited to wells and impounded surface supplies. It is rare to find either in flowing streams of normal $p$H and alkalinity In waters in the regions of acid mine drainage wastes, particularly along parts of the Allegheny and Monongahela rivers, where the $p$H is less than 5, there are significant quantities of both iron and manganese compounds in solution

From all the evidence available it appears that biologic activity is a powerful factor in the dissolving of iron and manganese.[269,277] It is apparent that anaerobic conditions must develop in order for appreciable amounts of iron and manganese to gain entrance to the water suppply.[275] For example, groundwaters that contain appreciable amounts of iron and/or manganese are always devoid of dissolved oxygen and are high in carbon dioxide. High carbon dioxide content indicates that bacterial oxidation of organic matter has been extensive, and the absence of dissolved oxygen shows that anaerobic conditions were developed.

Waters that normally do not contain any iron or manganese while flowing in a stream are certain to contain these compounds after the water has been impounded. The amount that goes into solution depends upon the character of the soil and the amount of plant life. Decomposition of organic matter in the lower strata of the water (hypolimnion) in the reservoir results in the elimination of dissolved oxygen and the production of carbon dioxide, so that the iron and manganese compounds in the flooded soil and rocks are converted to soluble compounds. These soluble compounds rise to the surface in those areas where the fall overturn occurs At this point they are oxidized and precipitated and then sink to the lower portion of the reservoirs where re-solution occurs in the absence of oxygen. Thus waters near the surface of reservoirs are most likely to be free from iron and manganese Therefore it is essential that multiple port outlet structures be provided for impounded supplies to allow selection of waters somewhere between the surface water containing algae and the deeper water (devoid of oxygen) that may contain iron and/or manganese. The amount of iron and manganese that gains entrance to either impounded surface supplies or groundwater varies throughout the country The manganese concentration in the hypolimnion of reservoirs varies from 2.0 mg/l in New Jersey to as much as 20 mg/l or more in the lakes of the Tennessee Valley Authority.[277] The time required for the appearance of significant amounts of iron and/or manganese in man-made lakes also varies with the location Some areas develop significant concentrations in one year, while others may require ten years

**Significance.** While there is no evidence that humans suffer from drinking water containing iron or manganese, these substances contribute to some of the most serious problems ever to confront the waterworks industry Waters containing ferrous bicarbonate stain everything with which they come in contact a yellowish to reddish brown Manganese-bearing waters free of iron will produce black stains. Waters containing ferrous bicarbonate usually contain some manganese, and this combination will produce stains varying from dark brown to black. Depending on the concentration of these compounds, consumers' complaints will start first with staining and streaking problems in the laundering process; next, there will be the red water or dirty water complaints; finally, there will appear large visible chunks of material that have sloughed off the distribution piping system. Most industrial wet processes, such as in the textile, pulp and paper, and the beverage industries, cannot tolerate this kind of water.

In addition to the physical phenomena of the presence of iron and manganese in the water, both contribute to and promote the growth of crenoform organisms in the distribution system. These filamentous organisms utilize both iron and manganese in their metabolism, and deposit within the pipelines to form heavy, gelatinous, stringy masses that slough off at intervals, causing a variety of problems for both domestic and industrial consumers. In addition to the unsightly mess that results, the growth of these organisms impairs the hydraulic carrying capacity of the entire system.

Because of the potential damage that these two elements can cause to a water supply system, the U.S Public Health Service Drinking Water Standards of 1962 have placed a limit of 0.3 mg/l of iron and 0.05 mg/l for manganese in potable water supplies. An AWWA task group[278] suggested limits of 0.05 mg/l for iron and 0.01 mg/l for manganese for an "ideal" quality water for public use. Traditionally manganese was reported as a combination with iron regardless of their ratio. Prior to the 1962 standards the limit was set at 0.3 mg/l for both iron and manganese. While 0.3 mg/l of iron could be tolerated under certain conditions this amount of manganese alone would cause severe difficulties. In view of the new standards, iron and manganese should be reported separately. Manganese in excess of 0.02 mg/l will almost surely cause problems in the distribution system. A large segment of waterworks people believe that all public water supplies should be devoid of manganese. While this is imperative for some industries, most domestic systems can tolerate up to 0.01 mg/l of manganese.

To emphasize the difficulty that may be encountered from these compounds it is pertinent to cite a classic example:

The Metropolitan Water District of Salt Lake City, Utah, has its source of supply water impounded at the Deer Creek reservoir on the Provo River. The pipeline from this reservoir to the distributing reservoir in Salt Lake City is some 40 miles long. The water is chlorinated at the outlet of the Deer Creek reservoir just as it enters the long pipeline. This treatment is for disinfection and prevention of slime growths in the long transmission line. A few years after this system had been in operation, it became coated with a black deposit of iron and manganese. When this coating is about $^{1}/_{32}$ inch thick it breaks off and colors the water. The manganese content is usually a few hundredths of a mg/l and sometimes goes as high as 0.1 mg/l but is continuous throughout the year. The outlet of the reservoir is at the bottom where the dissolved oxygen becomes depleted after spring turnover until it reaches zero. The source of iron and manganese in this water is due to the reducing conditions in the bottom of the reservoir, where both iron and manganese from the soil and biological life readily go into solution. After spring turnover, the iron and manganese rise to the top, where they are oxidized by the available dissolved oxygen in the water. This is followed by precipitation to the lower levels, where they again go into solution, only to become oxidized again by the chlorine and precipitate out in the pipeline. All types of chlorination programs were tried to eliminate this deposition. When chlorine was reduced, matters became worse because this resulted in a buildup of pipeline growths. Therefore the district has had to resort to pipeline cleaning on a regular basis. The solution to this problem is an outlet structure with the ability to withdraw water at selected depths to avoid the areas of iron and manganese concentrations. Unfortunately the present outlet structure is irrevocable.

## The Role of Chlorine

**Iron Removal.** Generally speaking, there are three methods for removing iron: by simple oxidation, by aeration or chlorination, or a combination of both; by precipitation with lime at a *p*H above 8; or by ion exchange. The major problem in these methods is the removal of the insoluble precipitate from each.

Chlorine, either free or combined, reacts to oxidize ferrous iron as follows:

$$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \longrightarrow 2Fe(OH)_3\downarrow + CaCl_2 + 6CO_2 \quad (6\text{-}22)$$

The soluble ferrous bicarbonate is oxidized to the insoluble ferric hydroxide, which can be removed by sedimentation and/or filtration, depending on how heavy a floc is produced. While this reaction will take place over a wide range of *p*H (4-10) the optimum *p*H is 7.0.[279] The colder the water, the slower are these reactions. This reaction takes a maximum of one hour, and is most rapid at *p*H 7.0. Each part of iron as Fe oxidized requires 0.64 mg/l chlorine. This reaction consumes 0.9 mg/l alkalinity as calcium carbonate ($CaCO_3$) for each mg/l iron as Fe oxidized.

If the iron present is in the complex organic form, free residual chlorine is more effective than combined in breaking up the iron complex so that oxidation by chlorine can proceed.

It is common practice to preaerate the raw water, which will oxidize some of the iron but, most important, will reduce the carbon dioxide content, causing a rise in *p*H where further oxidation by chlorine is more effective. While chlorine is usually applied after aeration, it is nearly always desirable to prechlorinate to control the crenoform organisms and to chlorinate again just after aeration for the further oxidation of the iron.

The application of chlorine to iron-bearing waters is imperative regardless of whether or not it is considered a part of the iron removal process, simply to prevent and control the growth of the crenoform organisms, which, if allowed to proliferate, can devastate the entire system and render the iron removal process useless. It should also be emphasized that when iron is present in small quantities (0.3 mg/l) where iron removal is not a factor, chlorine should be used to prevent the growth of the crenoform organisms, which have been known to proliferate in waters containing iron as low as 0.1 mg/l.

**Manganese Removal.** Chlorine will oxidize soluble manganous manganese to the insoluble manganic form as follows:

$$Cl_2 + MnSO_4 + 4NaOH \longrightarrow MnO_{2\downarrow} + 2NaCl + Na_2SO_4 + 2H_2O \quad (6\text{-}23)$$

The manganese dioxide produced may be removed by filtration as follows: Insoluble $MnO_2$ plates out on the sand grains. These deposits act as a catalyst to make possible complete extraction of manganese as $MnO_2$.

The optimum *p*H for this reaction is between 7 and 8. At *p*H 8 and with alkalinities on the order of 50 mg/l the time required may be two to three hours. As the *p*H increases, the time requirement diminishes to the *p*H values in the softening zone, where oxidation appears to be complete within minutes.[277,279] If the *p*H approaches 6.0, the time required may be as much as 12 hours. Temperature of the water does not appear to be a significant factor.

It should also be noted that manganese readily precipitates at *p*H 2 in heavy concentrations of chlorine. Proof of this is the troublesome deposit of manganese often found on the injector throats of chlorination equipment.

Chlorine in the form of free residual is imperative, and is in addition to that required to react with iron, ammonia, hydrogen sulfide, and so on. There should be 1.3 mg/l chlorine for each part of manganese as Mn.[279,280] For each part of Mn oxidized 3.4 mg/l alkalinity as $CaCO_3$ is consumed.

Difficulties from both iron and manganese are much more widespread than is commonly thought. Probably the most troublesome cases are those that are not readily categorized for physical removal of these compounds by an engineered treatment plant. Meyer[281] reported a number of such case histories. The end result is always the same: degradation of water quality in the distribution system; sloughing off of microbiological debris, and red or black water not fit to use. These cases occur throughout the United States. They are most common in underground supplies. The problem usually hits hardest those who can least afford to take proper corrective steps—the small rural community water supply or the individual well owner.

A typical case is a well that consistently contains less than 0.4 to 0.6 mg/l iron and probably 0.1 mg/l manganese. Most wells are capable of supporting troublesome growths of crenoform organisms, and so chlorine is applied to control these growths. Following chlorination there is likely to be a delayed reaction with chlorine and manganese. In such cases deposition of manganese in the remote or dead ends of the distribution system is common, indicating that ten to twelve hours are required for the complete oxidation of manganese. This problem can be overcome by adding a sequestering agent along with the chlorine as follows: Apply the chlorine down the well, ten feet below the pump bowls, as described in Chapter 9. Then add, at the rate of 2 mg/l sodium hexameta-phosphate down the well in the same line as the chlorine solution. This has been found in actual practice to be permissible, probably because there is not enough time for any reaction to set in between the additions of the chlorine and hexameta-phosphate. The latter will prevent the deposition of the manganese in the distribution system.

The procedure to follow for chlorination is: If the water by proper chemical analysis shows more than 0.3 mg/l iron, it should be chlorinated to prevent the growth of crenoform organisms. If there is more than 0.03-0.05 mg/l manganese present, it will probably precipitate out in a delayed reaction. If this occurs, add the hexametaphosphate as described.

This procedure has been known to be successful on iron contents as high as 0.6-0.8 mg/l and higher in some rare cases. Since chlorine is a must on any water over the iron limit, results will dictate whether or not the iron and manganese will have to be removed by a conventional treatment process.*

It should also be added that chlorination may be required in some instances where crenoform organisms proliferate when both iron and manganese are below the U.S. Public Health Service limits of 1962.

## Color Removal

The practice of free residual chlorination has been known to bleach true color in waters when color removal by coagulation and filtration has failed. The bleaching effect of chlorine is well known in swimming pool operation. An adequate free chlorine residual produces a polished, sparkling look to the water because of its ability to bleach organic matter.

True color removal by chlorine is most effective in the acid *p*H zone, between *p*H 4.0 and 6.8. Usually highly colored, low turbidity waters are either naturally acid or so lightly buffered that the application of chlorine may be sufficient to reduce the *p*H. In some cases the simple reduction of *p*H may cause the color to disappear. Therefore when decolorizing with chlorine, care must be taken so that when the upward readjustment of *p*H is performed for corrosion control it does not result in color return. This can be predicted by simple laboratory procedure.

Color removal by free residual chlorine is usually instantaneous, and temperature does not seem to be a factor. There is no rule for predicting the optimum dosage. The amount of color removal will vary with local conditions.[279]

When color is accompanied by turbidity, and coagulation is practiced, prechlorination to a free residual will aid materially in color removal by two means. The

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* See Chapter [illegible] the use of chlorine dioxide for iron and manganese removal.

first is through oxidation of part of the color, and the second is through its action as a coagulant aid. Thus two benefits may be expected: better color reduction, and decreased coagulant dosage.

In highly polished nitrified wastewater effluents White has observed that a free chlorine residual can produce a sparkling blue effluent, whereas the same effluent dosed with $NH_4OH$ to produce a combined chlorine residual shows a slight greenish-straw color. This demonstrates the bleaching ability of free chlorine.* So far as is known chloramine or other combined chlorine residuals do not have any bleaching power. If all else fails in an effort to prove that a chlorine residual is in fact a true free available residual and not some complex organic chloramine the bleaching quality of a free residual is certain proof.

## Chlorination of High *p*H Waters

A great many public water supplies are lime-softened resulting in *p*H values of 10 or more. One of the more notable sources of such supplies is the Missouri River. In the heavily populated areas along its course, the chemical and bacteriological characteristics of this water vary widely, which presents a formidable burden on the treatment plant. It is common practice first to soften the water with lime, which is followed by two-stage flocculation, coagulation, and settling. Chlorine is usually applied just ahead of secondary settling, followed by filtration and postammoniation.

Considerable bacteria reduction occurs in the softening process. Since the chlorine-consuming inorganic compounds of iron, manganese, and sulfur are largely removed by precipitation in the lime-softening process, the remaining chlorine demand is due primarily to nitrogenous compounds still in solution.

At *p*H 10 and higher, the reaction between free chlorine and the nitrogenous compounds is extremely slow. Temperature is also a factor. As the temperature drops, the chlorine ammonia reaction slows down. Fig. 6-23 illustrates the reaction of chlorine and lime-softened Missouri River water at St. Louis.[282] This water contained 0.9 mg/l ammonia nitrogen, and the temperature was 65°F. Note that after one hour's contact very little chlorine was consumed, and only after twenty-four hours did a typical free residual chlorine curve appear. Fig. 6-24 compares the chlorination of the same river water before and after softening when subjected to a sixty-minute contact period.

The importance of such application of chlorine is in the time factor. Even though the reactions between the chlorine and ammonia do not have sufficient time to go to completion within the treatment plant, there is a considerable benefit in a high free chlorine residual during this period. Chlorine doses of 5 mg/l lower the alkalinity approximately 7 mg/l, which may result in some lowering of the pH and tend to increase the efficiency of the free residual. Postammoniation is desirable to stablize the free chlorine residual for two reasons. At *p*H values above

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* When chlorine is used to bleach organic color the required dose may be as high as 15–20 mg/l.

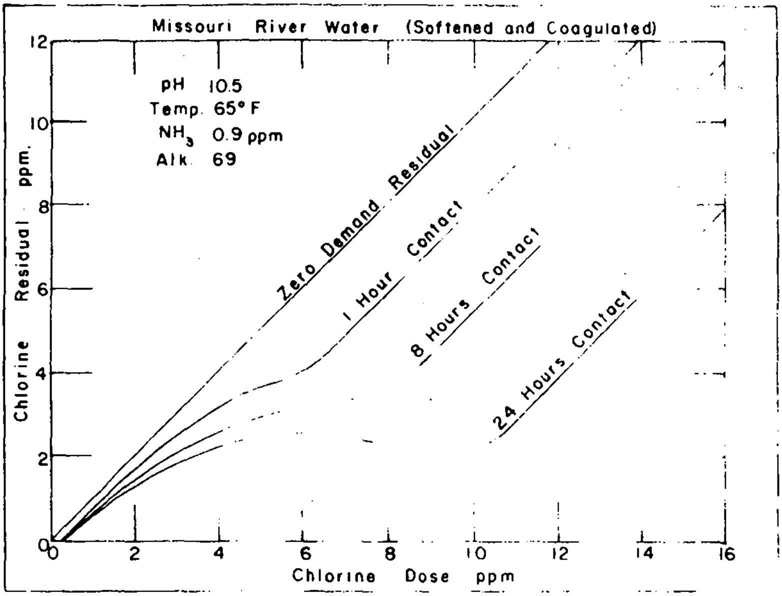


Fig 6-23 Relationship of chlorine and nitrogenous compounds in high-pH waters

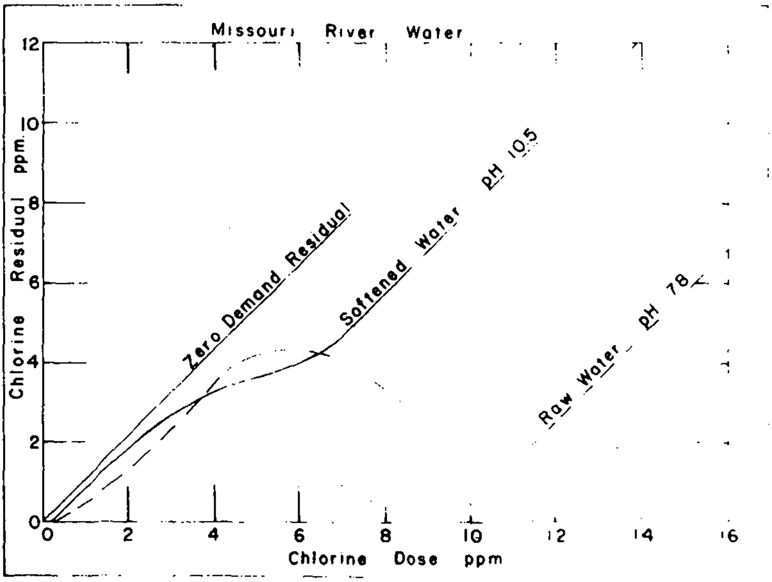


Fig 6-24 Comparison of chlorination of raw water and softened water

9, the efficiency of monochloramine is known to be superior to free chlorine. (See Chapter 4.) If the free chlorine residual were allowed to go into the distribution system, the continuing slow action of chlorine with the nitrogenous compounds already in the water could eventually, if given the proper amount of time, develop nitrogen trichloride and dichloramine, which could produce objectionable tastes and odors at the consumers' taps. Postammoniation prevents the formation of these compounds. The key to successful chlorination of high *p*H waters is a long residence time with free chlorine residual followed by postammoniation.

## Miscellaneous Applications of Chlorine

**Desalting Plants.** Current chlorination practice for desalinization plants has gradually evolved so that design engineers are providing pretreatment for the control of marine growths and the destruction of hydrogen sulfide and postchlorination for disinfection.

*Prechlorination.* Whenever seawater is used for any purpose, it will support and promote the various marine growths: mussels, sponges, bryozoa, and soft forms. Chlorination to control these growths can be on an intermittent basis, as in cooling water treatment. This treatment maintains plant capacity and prevents damage and plugging of tubular heat transfer equipment, thus avoiding costly downtime for repairs and cleaning.

An unexpected development has occurred at several desalinization plants: the appearance of hydrogen sulfide in the raw salt water. Its presence is attributed to decaying vegetation in tropical water supplies. If the supply is from deep wells, it is thought that the organic matter that gives rise to hydrogen sulfide, has been trapped in the coral growth.

The presence of hydrogen sulfide in a desalting plant using an evaporative technique is very costly because it will cause severe corrosion to almost any metal. Sometimes the $H_2S$ comes in slugs, making control difficult. It can be best eliminated by chlorination of the raw water unless the amounts present are excessive (>5.0 mg/l) when chlorination combined with aeration may be more economical.

*Postchlorination.* The freshwater effluent should be chlorinated as a safety precaution even though the U.S. Public Health Service recognizes the pasteurization effect of the evaporative techniques. At times in the operation of these plants when shutdowns occur, the freshwater system may become contaminated with the raw water. The treatment plant is by definition one huge cross-connection with a contaminated supply. For this reason most engineers include postchlorination in their plant design.

**Reflecting Pools.** It is common practice to include various kinds of water fountains to enhance the appearance of public recreation centers. These bodies of water require careful control to prevent the growth of any unsightly algae. At the same time the treatment must not give off any obnoxious chemical odors that would be offensive to the public.

These water systems usually contain cascades that provide a certain amount of aeration. It therefore is imperative that chlorination be maintained at a free residual level and that none of the chloramines be allowed to form. It is the chloramines, particularly dichloramine and nitrogen trichloride, which aerate out and cause offensive odors near the pool area.

The best way to treat these waters is to maintain a free chlorine residual of 0.75-1.25 mg/l continuously at a *p*H of 9.0-10.0 and never to use any algicide that contains nitrogen compounds. If proper free residual chlorination is practiced, algicides will not be required. The chlorination equipment, whether chlorine gas solution feed or hypochlorite, must be controlled by an amperometric residual analyzer calibrated for free chlorine residual. This will assist in preventing the formation of chloramines. The assurance of a *continuous* adequate free chlorine residual will eliminate the necessity of supplementing the chlorine treatment with an algicide.

All recirculated waters will require the continuous addition of caustic, sodium carbonate, or sodium bicarbonate to maintain the elevated *p*H when using chlorine gas, and most waters will require the addition of these chemicals even if hypochlorite is used. The latter may not add enough caustic to raise the *p*H to the required level except in waters softened by the lime soda process.

**Restoring Wells.** Most wells suffer from loss of efficiency with time. As the demand for additional water steadily increases, it becomes just as important to maintain efficiency of existing wells as it is to develop new wells.

There are several causes for the decline in well production: lowering of the ground water table; loss of pump efficiency, owing to worn, corroded, or encrusted parts, plugging of the aquifers by microorganisms and/or scale deposits; biofouling of the well screen area by microorganisms, fouling of the well screen area by deposits of scale and corrosion products or by mud, sand, and silt.

Natural phenomena bring about the deposition of scale and corrosion products and the proliferation of microorganisms that cause biofouling.

Water reaching the underground aquifers as rain picks up carbon dioxide. This is further supplemented by the evolution of carbon dioxide from decaying organic matter in the soil as the rain water penetrates into the earth. This addition of carbon dioxide greatly increases the solvent power of the water so that the potential scale-forming compounds are readily dissolved. The simple mechanical action of pumping a well causes a draw down of the static water level, which decreases the pressure in the vicinity of the well. This decrease in pressure plus the turbulence in the pump bowl area results in the release of carbon dioxide, which decreases the solubility of the water. Therefore it is at this point that the scale-forming compounds of calcium, magnesium iron and silica are deposited.

The existence of biofouling organisms in underground waters is well known.[283]

The prime offenders are the filamentous iron bacteria: *Crenothrix*, *Cladothrix*, *Leptothrix*, and *Gallionella*. Sulfur-bearing waters contribute to the filamentous organism *Begiattoa*. The area of the United States between Lake Michigan and Lake Superior to the north and to the Gulf of Mexico on the south has an overabundance of iron bacteria growing in underground supplies. The area immediately adjacent to Green Bay, Wisconsin, has earned a reputation of harboring the most lush growth of iron bacteria of any place in the United States and perhaps in the world. It is also known that a great many areas in the western part of the United States have underground waters that support troublesome growths of biofouling organisms deep within the aquifers. These areas include, but are not limited to, certain areas of the Rocky Mountains, the alluvial plains of Utah, and the Sacramento and San Joaquin valleys and the Los Angeles basin in California.

Two separate factors are involved in the restoration of well capacity 1) stimulation or redevelopment; 2) cleaning, reconditioning, and replacement of worn parts in the pump and ancillary devices.

Chlorine is used primarily in conjunction with other chemicals and methods involved in the stimulation procedure as a supplement following acid or polyphosphate treatment. It should always be used as a final chemical treatment before putting a well back in service, simply to eliminate contamination that may have resulted from the mechanics of the stimulation procedure. Erickson[284] has described the various methods in considerable detail. The methods used are dependent upon the nature of the problem and the type of aquifer involved.

The successful restoration of well productivity by chlorine alone was reported by Brown[285] in 1942. A group of four wells, with a total initial production of 7090 gpm, had deteriorated in four years to 3350 gpm. One treatment with superchlorine doses restored the total capacity to 6480 gpm, and the second chlorine treatment, a short time later, to 7200 gpm. Houston[286] reported (1946) on the use of heavy doses of chlorine to restore two wells that had lost 50 percent of their productivity. Chlorine treatment of 40 to 50 pounds of chlorine *down the well* was followed by several hundred gallons of muriatic acid to dissolve the scale and encrusted material.

Chlorine with dry ice for stimulation was reported by Suter[287] in 1938. This application to a well suspected of declining production due to biofouling completely restored the well to its original capacity.

The use of dry ice results in the evolution of carbon dioxide. This creates turbulence which mixes the chlorine and builds up a pressure that forces the heavily chlorinated water back into the aquifers. The use of dry ice, while inexpensive, is sometimes difficult to control. It has given way to other more modern methods using compressed air and vibratory explosions.[284]

The application of chemicals to effect a penetration is often done by the surging technique. This consists of pumping for ten to fifteen minutes at a time. As the pump is shut down, the water in the riser column upstream of the check valve surges back down into the well. This is repeated several times, and then the chlorine is allowed to "soak" in the well for twelve to twenty-four hours before being flushed out.

When a well is suspected of loss of productivity due to biofouling, there is no better way to alleviate this condition than with chlorine. It is not always a simple matter to prove that biofouling is the cause. The organisms responsible for these deposits belong to a group not ordinarily isolated in a routine sanitary water analysis. Many of them will not grow on the ordinary culture media employed; some of them are very difficult to cultivate on any media; and they are seldom dispersed in the water in appreciable concentration.

For the destruction of the iron bacteria group (*Crenothrix. Leptothrix. Clonothrix,* and *Gallionella*), a 200 mg/l concentration in the well is effective. The destruction of sulfur bacteria may require as much as 500 mg/l. The chlorine should be applied down the well ten feet or so below the pump bowls and, after the stimulation procedure, be allowed to soak for several hours before flushing. If scale and corrosion deposits are known to exist in the well screen and adjacent areas, the chlorine may be supplemented with acid after first applying an acid inhibitor to protect against corrosion of the metal parts.

When using chlorine for the elimination of biofouling organisms, there is the danger of oxidizing ferrous compounds to ferric hydroxide, which might result in the formation of gelatinous flocs that would settle out in the well only to cause some plugging at a later date. If investigation reveals that this might be a factor, polyphosphates are used along with the chlorine to sequester the formation of ferric precipitates. However, care must be exercised in the use of polyphosphates. In wells with multiple screens in water-bearing strata separated by clay or shales, the action of polyphosphates on these materials will cause the disintegration of the clay and shales, which will infiltrate the sand and gravel strata and tend to reduce the productivity of the well.

The treatment of some biofouling problems occasionally calls for sterner and more costly methods of chemical treatment. Piatek[288] reported (1967) that attempts at Sayreville, New Jersey, to control such fouling in the screens, riser column, and transmission line required such long periods of high dosages of chlorine that a corrosion problem developed. The problem was solved by separating the cleaning procedure into two parts: one for the well and riser column, and the other for the transmission line. Chlorine dioxide was used instead of chlorine. In this case the chlorine dioxide was produced by combining hypochlorite with an aqueous solution of anthium dioxide. This mixture was added along with a polyphosphate. For an 8-inch well containing forty feet of water and 20 feet of air space, a solution of 100 pounds of Calgon in 50 gallons of water was followed by 5 pounds of 70 percent hypochlorite dissolved in 5 gallons of water. This solution was surged once in the well to assure a good mix, and then 15 gallons of anthium dioxide were added. This total mixture was surged for two hours by pumping fifteen minutes and shutting down for fifteen minutes, and repeating. Then it was allowed to stand overnight. This was repeated every two months. Such experiences indicate the necessity of continuous treatment with both chlorine and polyphosphate added down the well at nominal dosages for the continuous destruction of the organisms that cause fouling in the system elsewhere than in the aquifers.

**Injection Wells.** Reclaimed or other waters are being used more and more to replenish the underground aquifers in those areas that are short of water supply. Injection wells are also used extensively for maintaining oil well production,[289] and for the prevention of sea water intrusion of freshwater aquifers as well as to prevent land subsidence due to withdrawal of oil from underground deposits.

It is the consensus[289,290] that any water used for injection into underground aquifers should be sterilized--free of bacteria. This will provide protection from the growth of filamentous organisms that might plug the aquifers, and will also inhibit the growth in the aquifers of bacteria native to the underground formation that might otherwise proliferate owing to the introduction of a water containing oxygen and nutrients essential to their growth.

It may be appropriate for users of injection water to establish a very high initial chlorine dosage to provide several mg/l free chlorine residual and then taper off to 1.5 mg/l.[290]

## Disinfection of Water Mains and Storage Tanks

Chlorine is used exclusively in the disinfection of both water mains and storage tanks. It can be applied as an aqueous solution from chlorine gas in cylinders, as a hypochlorite solution from either granular calcium hypochlorite, or liquid sodium hypochlorite, or as calcium hypochlorite in the tablet form

When using chlorine gas from cylinders, it is imperative that a conventional chlorinator with injector and booster pump be used. Otherwise, the handling of the chlorine gas can be awkward and hazardous.

Calcium hypochlorite contains 65 percent available chlorine by weight in the granular or tabular form. The tablets, 6 to 8 to the ounce, are designed to dissolve slowly in water. Calcium hypochlorite is dissolved into water to make about a 1 percent (10,000 mg/l) solution, which is injected into the main.

Sodium hypochlorite is packaged in strengths from 5.25 to 16 percent available chlorine. It is available as a liquid in containers varying in size from one-quart bottles to five-gallon carboys, and may also be purchased in bulk for delivery by tank truck in some locations.

**Water Mains.** The hypochlorite solutions are usually injected into water mains by gasoline- or electric-powered chemical feed pumps or by hand pumps. Special pumps designed to handle only hypochlorite solutions are not mandatory. Ordinary cast iron pumps give many hours of satisfactory operation if they are properly flushed and cleaned after each use period. Hand pumps are also satisfactory

The methods of applying chlorine to water mains are continuous-feed, slug-dosage, and tablet. These are described in detail in the AWWA committee 8360D report.[291] The AWWA standard for the continuous-feed method calls for chlorination to continue until the entire main contains chlorine solution. The recommended dosage is 50 mg/l, but the requirement is to have no less than a 25 mg/l residual throughout the entire length of the main at the end of twenty-four hours.

For large systems, the slug method is used. This consists of a slug or column of water containing a concentration of at least 300 mg/l to expose all the interior surfaces for a period of at least three hours.

The tablet method is limited to short extensions (up to 2500 feet) and smaller diameter mains (up to 12 inches). Because the preliminary flushing step must be eliminated, this method should be used only when scrupulous cleanliness has been maintained.

Table 6-6 gives the amounts of chlorine required for various size pipes. Table 6-7 shows the number of hypochlorite tablets required.

The confirmation of adequate disinfection is by proper bacteriologic tests made after final flushing.

The recommended procedure for chlorine residual determination is the drop dilution method using acid O-T as the reagent. (See Chapter 5.)

**Storage Tanks.** The disinfection of elevated tanks, covered ground storage tanks, and ship tanks is achieved most conveniently by the use of portable chlorination equipment. The chlorine solution is added at the rate of 50 mg/l while the tank is being filled.

Portable chlorination equipment must be used carefully and under expert supervision. A typical arrangement, as reported by Tracy,[292] consists of limiting the solution strength to 500 mg/l using a 25 gpm pump with 100 feet of 1-inch chlorine solution hose terminating in a PVC spray nozzle. All workmen must wear oxygen type

Table 6-6 Chlorine Required to Produce 50 mg/l Concentration in 100 feet of Pipe by Diameter

| *Pipe size (in)* | *100 percent chlorine (lb)* | *1 percent chlorine solution (gal)* |
|---|---|---|
| 4 | 0.027 | 0.33 |
| 6 | 0.061 | 0.73 |
| 8 | 0.108 | 1.30 |
| 10 | 0.170 | 2.04 |
| 12 | 0.240 | 2.88 |
| 18 | 0.483 | 5.80 |
| 24 | 0.875 | 10.10 |
| 36 | 2.220 | 26.50 |

Table 6-7 Number of Hypochlorite Tablets of 5 g Required for Dose of 50 mg/l*

| *Length of section (ft)* | *Diameter of pipe (in)* 2 | 4 | 6 | 8 | 10 | 12 |
|---|---|---|---|---|---|---|
| 13 or less | 1 | 1 | 2 | 2 | 3 | 5 |
| 18 | 1 | 1 | 2 | 3 | 5 | 6 |
| 20 | 1 | 1 | 2 | 3 | 5 | 7 |
| 30 | 1 | 2 | 3 | 5 | 7 | 10 |
| 40 | 1 | 2 | 4 | 6 | 9 | 14 |

* Based on 3¾ gm available chlorine per tablet.

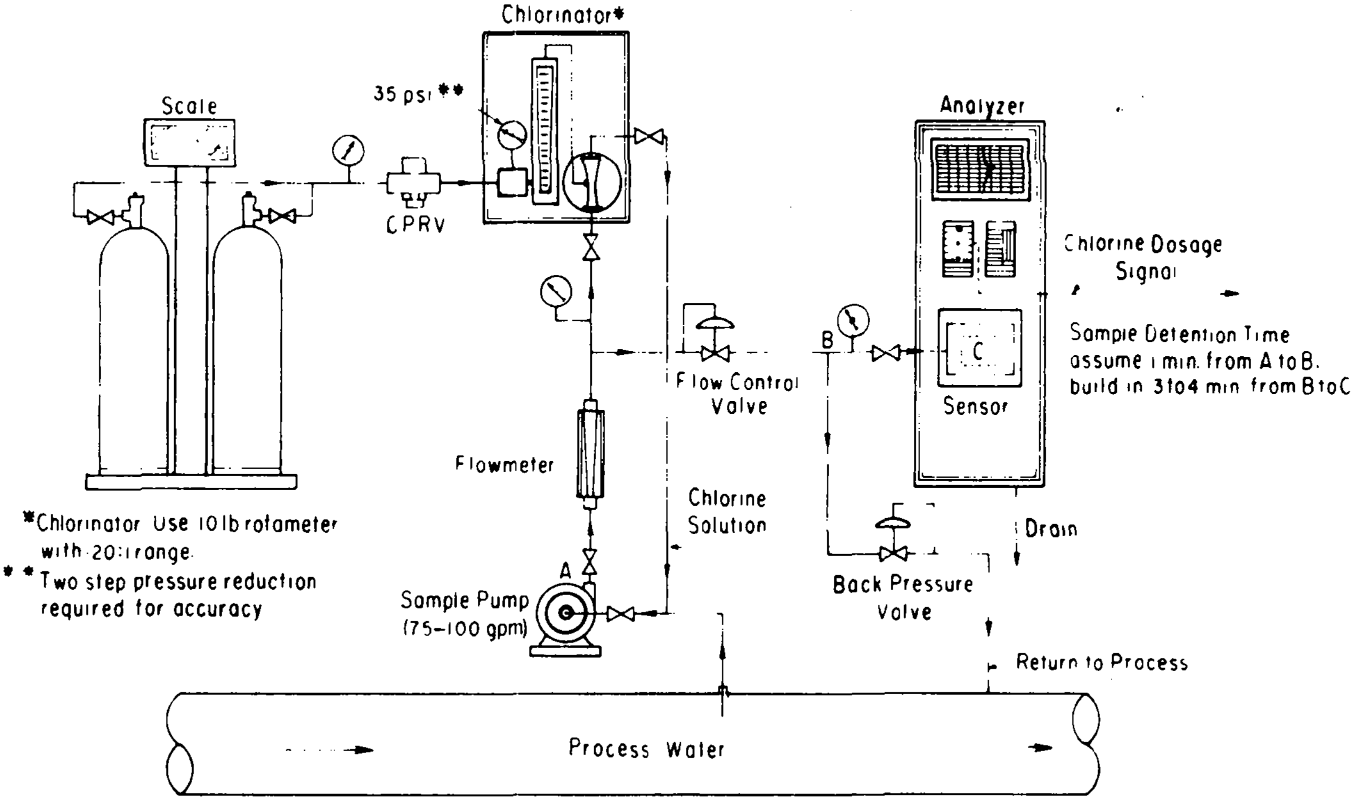
gas masks, and operators in the tank will require raincoats as well. This operation requires three men, changing nozzle operators every twenty minutes. While it is an uncomfortable job, it is not particularly hazardous. The washing operation is carried out with all the valves closed. All of the chlorine solution will flow to the bottom, and any particulate matter will be carried along or sink to the bottom in the strong chlorine solution. This is then flushed from the reservoir after the washing is completed. Washing reservoirs with hypochlorite solutions is awkward and cumbersome. The use of chlorine solution from portable equipment is not only less expensive but can accomplish the task in a much shorter time.

## Summary of Recommendations to Achieve the Objectives of Chlorination

**Chlorine Demand.** This is a significant water quality parameter and should be monitored continuously as shown in Fig. 6-25. The potential for THM formation is partly a function of chlorine demand. This parameter is a measure of pollution and is related to the presence of nitrogenous compounds. These compounds play an important role in the chemistry of chlorination.

When the ammonia nitrogen content in untreated water reaches 0.15 mg/l and organic nitrogen content of 0.20 mg/l, routine chlorine demand studies as described by Feben and Taras (Chapter 4) should be started. From these studies each water producer can establish chlorine demand constants which will provide a more rational control over the application of chlorine. Furthermore these studies will provide a historical background of raw water quality.

*Controlling THMs.* For the long-term, the most effective way to control THMs is to exploit pretreatment practices which would improve the quality of the raw water before chlorination. These practices should be patterned after current European and U.K. methods. The objectives of pretreatment should be as follows: 1



*Chlorinator Use 10 lb rotameter with 20:1 range.
* * Two step pressure reduction required for accuracy

Fig 6-25 Continuous chlorine demand monitoring system.

maximize THM precursor removal, 2) reduce ammonia-N concentration to 0.10 mg/l, 3) reduce organic-N concentration to 0.05 mg/l, 4) limit 15 min chlorine demand to 0.5 mg/l. These guidelines should improve raw water quality sufficiently to allow the use of the free chlorine residual process without exceeding the EPA MCL for THMs; i.e., 50 $\mu$g/l.

**Chlorine Residual Analysis.** When using the free residual process it is customary to monitor and control on the basis of the free residual fraction. This is not enough. It is suggested that whenever the chlorine residual analyzer is calibrated, a forward amperometric titration for all three fractions (free, mono-, and dichloramine) should be carried out. The best results from the free residual process obtain from a total residual that contains *85 percent free available chlorine* (HOCl).

**Nitrogen Trichloride Formation Spells Trouble.** Nitrogen trichloride can be generated in copious quantities during the free residual process in some waters. These waters are usually highly polluted with organic nitrogen compounds derived usually from wastewater discharges. Typical conditions for $NCl_3$ formation at *p*H levels of 7–9 require a chlorine to ammonia ratio of about 12 : 1, ammonia-N concentration 0.5 mg/l or greater, and organic N concentration 0.3 mg/l or greater. The higher the concentration of the nitrogen compounds, the greater the production of $NCl_3$. This compound produces a pungent geranium like odor at low concentrations (0.02 mg/l). However it is practically insoluble in water and is difficult to measure by available methods. Owing to its pervasive and unmistakable odor, and its characteristic eye tearing quality, it is not necessary to attempt detection with analytical methods. Therefore those waters subject to developing significant amounts of nuisance residuals (greater than 20 percent of the total chlorine residual) should be able to generate $NCl_3$, which is easily scavenged by postaeration. This will also reduce the dichloramine fraction well below the taste and odor producing level. Nitrogen trichloride aerates easily and decomposes rapidly in sunlight. This ability to decay rapidly in the atmosphere, including the hours of darkness, reduces significantly the possibility of it becoming an air pollution problem.

**Points of Chlorine Application.** If it is practical, use only a single point of application—at the influent of the treatment process—and in a sufficient amount to maintain a free chlorine residual throughout the entire treatment train. When this is not possible, a secondary point of application must be provided. This one is usually just ahead of the filters.

**Monitoring Residuals.** The chlorine residual should be monitored continuously in vital parts of the treatment process. It should not be limited to the plant effluent. For example, in addition to the analyzer controlling plant effluent residual, an accessory analyzer should record residuals at the influent of the sedimentation basins and filter influent. The sample pumps from each of these locations should operate continuously one to the analyzer cell and the other to waste via a three-way valve This three way valve reverses the flow pattern at a predetermined interval by means of a time clock For ten minutes, the sample should flow through the analyzer from the sedimentation influent sample pump; the time clock would then actuate the three-way valve, diverting the flow from the other sampling point (filter influent) from waste overflow to the chlorine residual analyzer This procedure will produce two monitoring traces of chlorine residual in vital parts of the plant. The first would be a guide as to the sufficiency of the prechlorination dosage. The second would indicate whether or not sufficient chlorine was present to provide an adequate residual in the effluent This situation would also protect the filter media from biofouling

Residuals should also be monitored in the distribution system. The preferred locations are at trouble spots where there may be degradation of water quality, insufficient chlorine residual, and/or consumer complaints.

Monitoring stations in the distribution system will help determine both the need and location of relay chlorination stations.

**Controlling the Chloramine Process.** This process carries with it the potential to supply the treated water with nutrients that promote the proliferation of bacteria and other microorganisms which conspire to degrade the quality of any potable water These nutrients will become available when the chloramine residual is consumed At this point the chloramine reverts to ammonia nitrogen. If chlorine is added when the residual is depleted, the ammonia nitrogen is immediately converted to chloramine This is the reason for chlorine relay stations. Chloramination systems must be designed and operated so that measurable chloramine residuals persist continuously throughout the distribution network.

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# 9
# Chlorine Facilities Design

## PREFACE

The conventional chlorination facility for use in potable water and wastewater treatment consists of three principal parts: chlorine supply, metering system, and injector system. In addition there is ancillary equipment: safety equipment, metering and control instrumentation and chlorine residual analyzers.

## CHLORINE SUPPLY SYSTEM

Chlorine is packaged in special steel containers of various sizes, as follows:

1 100- and 150-lb cylinders
2 Ton containers
3 Single-unit tank cars
4 Multiple-unit tank cars (TMU) containing fifteen 1-ton cylinders
5 Tank trucks of 15–20 tons capacity
6 Stationary storage tanks

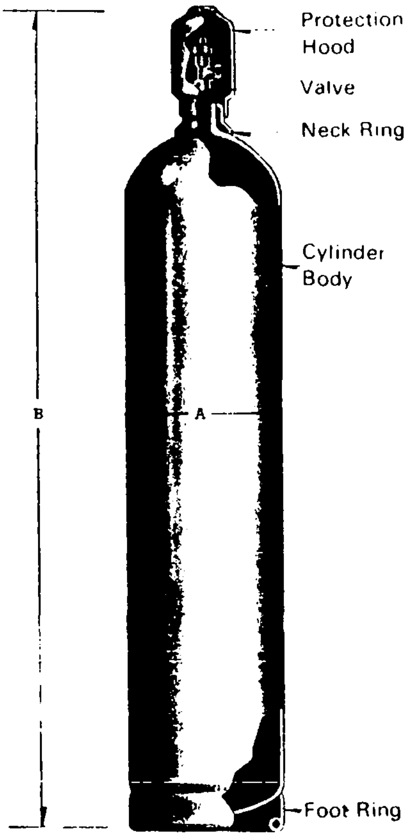
The selection of the various sizes is discussed in this chapter.

**100- and 150-lb Cylinders.** The pertinent dimensions and tare weight of these containers are shown in Fig. 9-1.

Minor variations in these dimensions depend upon the cylinder age and the manufacturer The 150-lb cylinder is so popular that the 100-lb size may be considered obsolete Some packagers have available a 35-lb cylinder, which is suitable for laboratory or test work on a small scale.

The packager fills these cylinders with liquid chlorine to approximately 85 percent of total volume, the remaining 15 percent is occupied by the chlorine gas. There must be strict adherence to these figures in order to prevent hydrostatic rupture of the cylinder in the event of abnormally high ambient temperatures. As the temperature rises, the liquid chlorine expands. Theoretically, the cylinder could get hot enough to completely fill the remaining 15 percent occupied by gas and

**Chlorine Cylinder**



| Net Cylinder Contents | Approx. Tare, Lbs.* | Dimensions, Inches | |
|---|---|---|---|
| | | A | B |
| 100 Lbs. | 73 | 8¼ | 54½ |
| 150 Lbs. | 92 | 10¼ | 54½ |

*Stamped tare weight on cylinder shoulder does not include valve protection hood

Fig. 9-1 Chlorine cylinder dimensions (courtesy PPG Industries, Chemical Division) therefore rupture the cylinder. However, the outlet valve on these cylinders is fitted with a fusible plug, the core of which will melt at approximately 158°F, thus preventing rupture of the cylinder during instances of abnormally high temperatures. When the plug melts, the liquid chlorine discharged through the core opening (1/8" diameter) cools so rapidly that it freezes, momentarily halting the flow of liquid chlorine. By this time the danger of cylinder rupture is over, and a trained operator wearing air or oxygen breathing equipment can apply the chlorine safety kit, stop the leak, and remove the cylinder from the area.

The gross weight of a full 150-lb cylinder varies from 250 to 285 lb. Therefore these cylinders are best handled by a two-wheel cylinder handtruck. *Never use slings, or try to pick up cylinders with hoisting equipment attached to the protective cap or valve.* The water volume of a 150-lb cylinder is 14.4 gallons.

The most important design considerations are as follows:

1. Direct sunlight must never reach the cylinder.
2. The maximum withdrawal rate should be limited to 40 lb/day/cylinder.
3. Minimum allowable room temperature is 50°F.
4. Heat must never be applied directly to the cylinder.
5. Sufficient space should be allowed in the supply area for at least one spare cylinder for each one in service.

Provisions should be made so that the operator can determine the amount of chlorine left in the supply system. This is most effectively done by weighing scales.

Figure 9-2 illustrates a new concept in scales for weighing 100- or 150-lb chlorine cylinders. This is Capital Controls Co. Series 1350 LO Line Digital scale. It has a low-profile platform which transfers the cylinder weight to a strain gage transducer. The electronics package within the scale system provides a digital readout in pounds of chlorine remaining (or kilos). This system is unique because it can also provide a 4-20 mA output signal to a timer, which can then convert loss of weight at the scale into a chlorine flow rate. This replaces the usual chlorine gas-flow transmitters. The weighing accuracy is claimed to be ±0.5 percent of capacity (±0.75 lb for a 150-lb cylinder).

There are individual weighing surfaces for each cylinder which can be arranged to handle two banks of cylinders. There can be from one to six cylinders per bank. This is equivalent to a maximum of 900 lb chlorine exclusive of tare weight. There is a 3-digit readout and a summator readout for each bank of cylinders plus a mechanism to adjust out the tare weight for each cylinder.

Automatic switchover devices are readily adapted to this scale regardless of the number of cylinders in each bank.

Ideally the chlorine supply system should always be at a lower temperature than the chlorinator when withdrawal is from the gas phase. This reduces the possibility of reliquefaction at the chlorinator. The distance between the chlorine supply and the chlorinator should always be as short as conveniently possible.

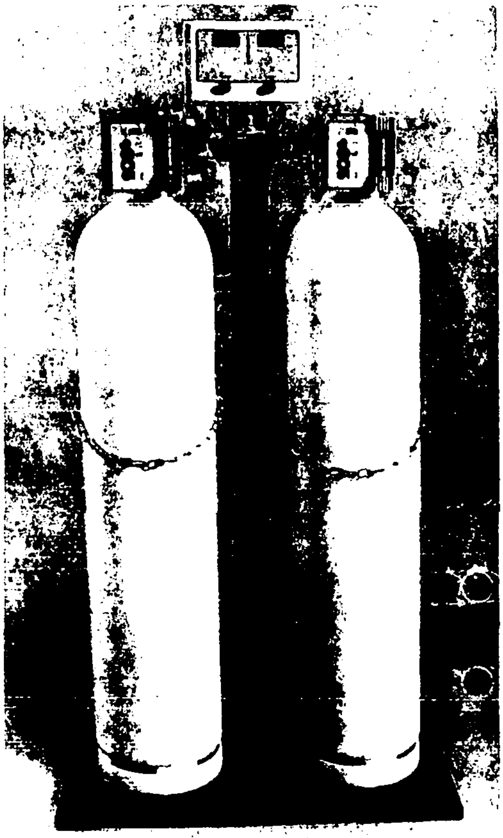


Fig. 9-2 Two cylinder digital scale with output signal (courtesy Capital Controls Co.).

The greatest difficulty in operating such installations is caused by reliquefaction of the chlorine gas. This occurs mostly at the first point of pressure reduction; when it occurs, impurities in the chlorine gas are deposited at this point, which is the chlorine inlet pressure-reducing valve of the chlorinator. This phenomenon is a result of the hot gas in the cylinder passing very slowly (inches per hour) through the piping between the cylinder and chlorinator and cooling during the night. This cooling causes the gas to reliquefy. The amount and frequency of trouble depends upon how much cooling takes place. This is a function of the difference in ambient temperatures between day and night, the volume of gas between cylinder and chlorinator, and the velocity of gas flow. The lower the feed rate and the greater the distance between cylinder and chlorinator, the greater the chance of reliquefaction, other things being equal. Reliquefaction will not occur if the cylinder is kept cooler than the chlorinator. This brings up the necessity for some type of insulation, which will be discussed below in this chapter.

The minimum allowable temperature for the chlorine storage area is about 50°F. Below this temperature the flow of chlorine becomes sluggish and erratic, particularly for smaller installations, from 1 to 20 lb/day. Therefore all 150-lb cylinder installations utilizing one or two cylinders should be housed in adequately insulated areas with provision for heating to 65°F.

Heat should never be applied directly to a chlorine cylinder. Steel will ignite spontaneously at about 483°F in the presence of chlorine. For example, it is possible to "burn" a hole in a chlorine cylinder by directing the rays of an infrared lamp onto the cylinder at the liquid level. With heat on one side, the liquid chlorine on the other side acts as a catalyst and will support the burning of the steel until the chlorine has become exhausted.

Sufficient space should be allowed for the scale and storage for one spare cylinder for each one connected in service. The distance between the cylinders should be sufficient so that standard four-foot flexible connections can be used. Each cylinder hookup should consist of an auxiliary cylinder valve and flexible connection.*

Filters and traps ahead of all chlorinator control apparatus are highly desirable, to prevent the impurities inherent in chlorine from reaching the chlorinator control mechanisms. Most small chlorinators have a built-in strainer of some type, which should be preceded by a convenient inlet trap.

If the storage area for in-service cylinders is properly designed, external chlorine pressure-reducing valves are not required. If the location of these cylinders is remote, an external reducing valve should be installed as close as possible to the cylinders.** If the chlorine supply line is longer than ten or fifteen feet and is subject to much variation in temperature due to poor insulation from ambient temperature changes, an external chlorine pressure-reducing valve should be installed close to the cylinders to avoid reliquefaction. If the vapor pressure in the chlorine cylinder is 100 psi, the gas between the cylinder and the chlorinator will reliquefy if the temperature drops below 80°F. If a reducing valve is utilized to reduce the pressure from 100 to 40 psi, the temperature would have to drop to below 32°F before reliquefaction will occur. (See Chapter 1.)

**Automatic Switchover.** The ability to switch from an empty cylinder to a full cylinder automatically increases the reliability of any chlorination system. Automatic switchover devices can perform in pressure systems or vacuum systems.

For systems up to 500 lb/day the vacuum system is ideal. A typical system is illustrated in Fig. 9-3. The vacuum regulator check units shown adjacent to the cylinder may be located remotely from the chlorinator, e.g., for separate housing location of cylinders.

The system functions as follows. Gas under pressure enters the vacuum regulator

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* [illegible] systems do not require flex connections nor auxiliary cylinder valves. Neverthe- [illegible] reliquefaction.

** When [illegible] are used, external pressure reducing valves may be required to provide [illegible] owing to ambient conditions.

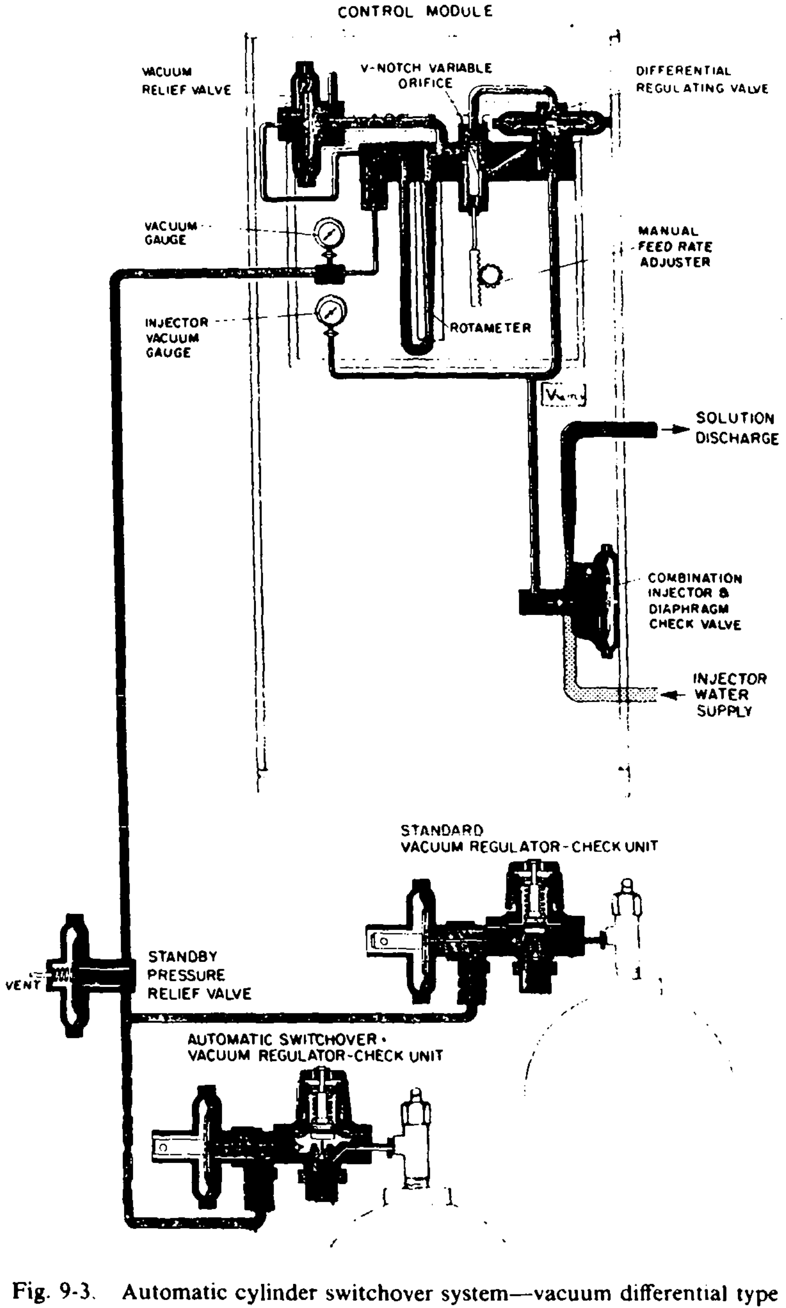

Fig. 9-3. Automatic cylinder switchover system—vacuum differential type (courtesy Wallace and Tiernan Div. Pennwalt Corp.)

check unit As the gas flows through the two valves the cylinder pressure is reduced to the vacuum in the system created by the chlorinator injector The valves will not open unless the minimum operating vacuum is produced (approx 10 in Hg) Flow of gas will be indicated by a depressed red indicator button If the first valve allows gas to flow when a vacuum is not present, the second valve will remain closed and contain the pressure in the vacuum regulator check unit, which is designed to contain full container pressure These vacuum regulator check units are fitted with mechanical latches called "detentes." One valve remains open until the cylinder or cylinders connected to this valve are exhausted This situation allows the operating vacuum to rise significantly higher than normal (≈ 3–5 in Hg). This rise in vacuum level provides sufficient force to unlatch the second unit which then takes over the gas supply function.

For safety reasons a standby pressure relief valve must be installed as shown in Fig. 9-3. This valve must be vented to atmosphere well above ground level.

Positive pressure systems are described later in this chapter.

## Ton Containers:

*General Discussion.* Unlike the 150-lb cylinders, either gas or liquid may be withdrawn from ton containers; consequently each container has two outlet valves. Also unlike the small cylinders, the ton containers have six fusible plugs—three in each of the dished heads. Fig. 9-4 illustrates the ton container. They are transported either by truck (Fig 9-5) or by multiple-unit tank cars (TMU). A truck can carry a maximum of fourteen containers; a TMU, fifteen, as shown in Fig. 9-6 *The water volume of a ton container is 192 gallons.*

The gross weight of these containers (3500 lb) dictates that proper handling equipment must be used The container is designed for use in the horizontal position. Each cylinder must be positioned so that the outlet valves line up in the vertical before being connected to the supply system In other words, the container must

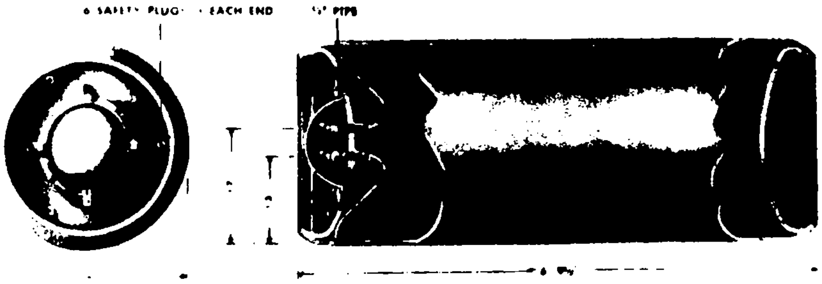

Fig. 9-4 Ton container for chlorine (courtesy Chlorine Institute)

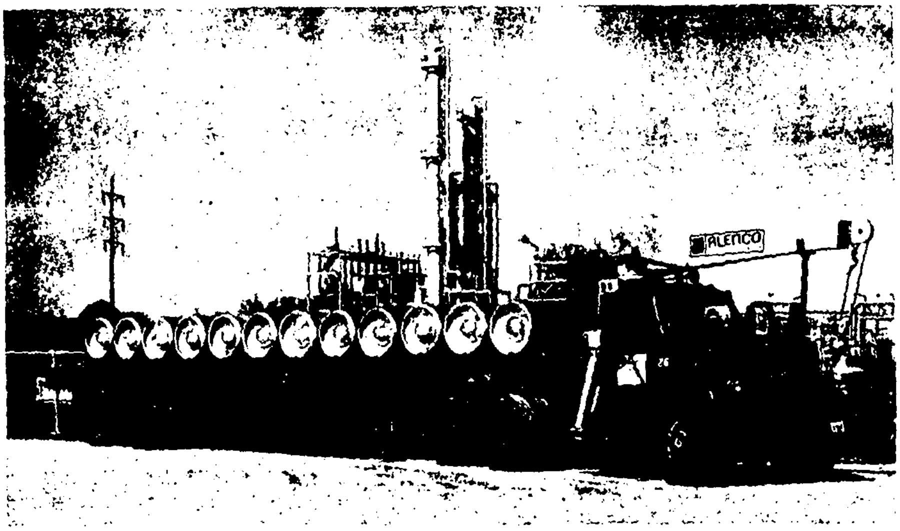

Fig. 9-5 Ton container truck and trailer rig with boom (courtesy PPG Industries, Chemical Division)

be positioned so that one eductor tube is in the gas position and the other in the liquid when the container is full.

*Handling Equipment.* Proper handling equipment includes the following:

1 Two-ton capacity electric hoist
2 Lifting bar
3 Cylinder trunnions
4 Monorail for hoist
5 Cinch straps*

A good example of proper handling equipment is shown in Fig. 9-7.

Not only must the cylinders be moved from transport to supply position; it is most important that each cylinder to be connected be easily rotated in order to align the outlet valves vertically. This is accomplished by a pair of trunnions (Fig. 9-8), which serve not only as a method of positioning the outlet valves but also for the spacing and support for each cylinder. Further, if the trunnion is properly designed, it should function to contain the cylinder in the event of a collision with an incoming cylinder on the traveling hoist, and to prevent an empty cylinder from rotating without an external force of at least 15 ft lb.**

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* Where seismic forces are of concern, plastic cinch straps should be used to prevent the cylinder from becoming dislodged from the trunnions.[70]

** A recent earthquake with the epicenter at Livermore CA and a 5.8–6.2 Richter force failed to move banks of ton containers at two wastewater treatment plants nearby. Plant container alignment was 90° different from each other

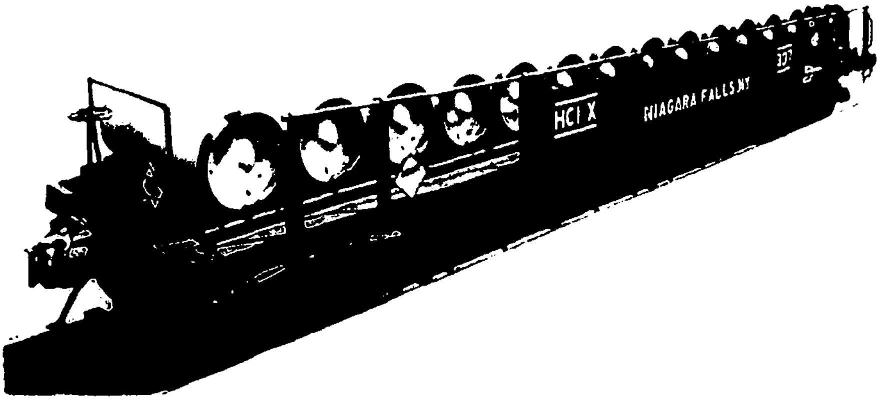

Fig 9-6 TMU car (courtesy Chlorine Institute).

One of the critical design dimensions for ton container installations is the distance from the bottom of the monorail to the floor of the container room. The monorail must be high enough to pick up a cylinder off the truck and also high enough to lift one cylinder over another that is on the floor. Usually the governing distance

Fig 9-7 Typical chlorine storage with trunnions for rotation and spacing of ton containers (courtesy Chlorine Specialties, Inc.)

Fig. 9-8 Trunnion for ton container (courtesy Chlorine Specialties Inc.)

is the height of the truck bed above the container floor Fig. 9-9 illustrates how to arrive at the minimum distance of the monorail above the floor

*Gas Withdrawal.* Space requirements depend upon whether the cylinders are for liquid or gas withdrawal, the rate of withdrawal, the quantity price break for the number of cylinders delivered at one time, and the length of time containers can be used without incurring demurrage charges

At room temperature the maximum gas withdrawal rate from a ton cylinder is approximately 400 lb/day. If the maximum chlorinator capacity is 400 lb/day, then one cylinder in service will suffice. If it is a 500 lb/day unit, two ton cylinders must be in service simultaneously. Theoretically, gas withdrawal can be used up to any capacity if enough cylinders are connected to the supply header Switching from gas withdrawal to liquid withdrawal utilizing an evaporator is necessary when a continuous rate of 1500 lb/day is reached. The one exception to this rule of thumb is in intermittent operating installations, as employed on cooling water circuits At such installations it is customary practice to withdraw rates up to 1000 lb/day for thirty minutes if the temperature of the storage area never goes below 50°F In warmer areas 1500 lb/day gas withdrawal is safe up to one hour from a single ton cylinder This assumes a temperature-pressure restoration period of no gas withdrawal of at least twice the length of time as the withdrawal period.

For up to 1500 lb/day maximum continuous withdrawal, space should be provided for four cylinders in simultaneous service, four standby cylinders, and four empty spaces for the next delivery Beyond this rate, an evaporator should be installed. However, there is one exception, as follows

In hot climates where the "in shade" summer temperatures exceed 95 to 100°F on a consistent basis it is desirable to consider the use of an evaporator Normally those climates experiencing summer temperatures of 100°F usually experience winter temperatures of 15°F Therefore, the evaporator concept takes care of both extremes of climatic temperature Liquid withdrawal of chlorine to an evaporator from a supply system is least affected by ambient temperature The only precaution is to prevent direct sunlight on the cylinders For winter operation no special

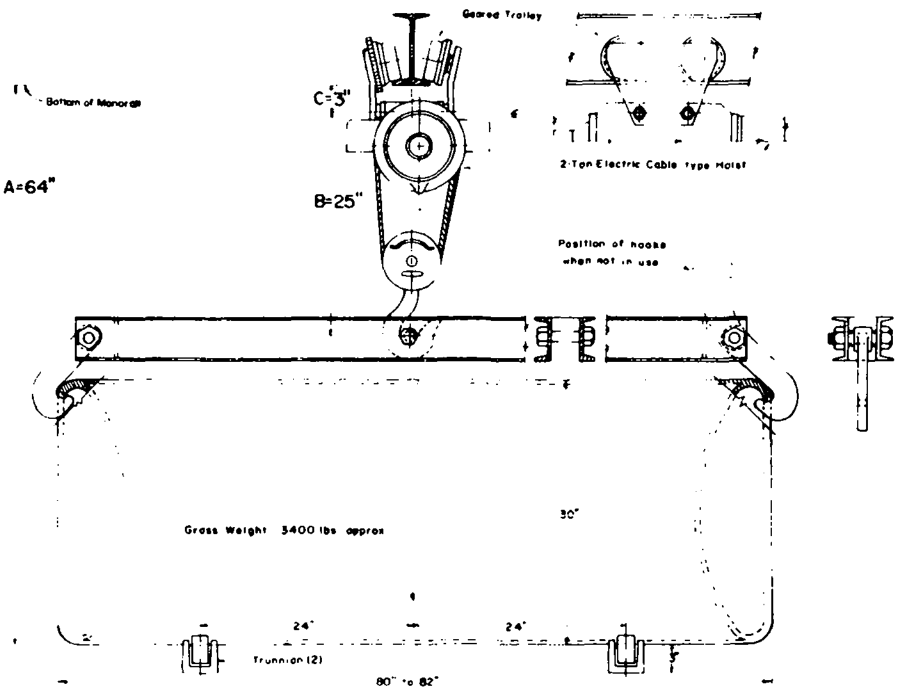

Fig. 9-9 Monorail height location To determine monorail height above grade add truck bed height to distance "A" as illustrated. Check dimensions "B" and "C" with hoist manufacturer (courtesy Chlorine Specialties Inc.)

precautions are required (such as artificial heating) because the gas temperature at the outlet of the evaporator will usually *exceed* 100°F regardless of room temperature and the temperature of the gas in the vacuum line to the injector will never fall below the critical temperature (35°F) where chlorine hydrate occurs.

Evaporators are available in capacities of 4000 lb/day, 6000 lb/day, and 8000 lb/day. In a pinch, one cylinder can discharge liquid to an evaporator at a rate as high as 12,000 lb/day This means that an evaporator can be used to conserve space for cylinder storage if necessary The optimum storage requirements should be based on the quantity discount price break that is offered by the local chlorine supplier This usually occurs at a quantity of five, thus dictating space for five in service, for five empties, and a vacant space for the incoming five, or a total space for fifteen ton cylinders

If the gas phase is used, the same consideration must be given to the design of ton cylinder storage space as for 150-lb cylinders. All ton cylinder installations using gas withdrawal should be equipped with a special filter installed as close

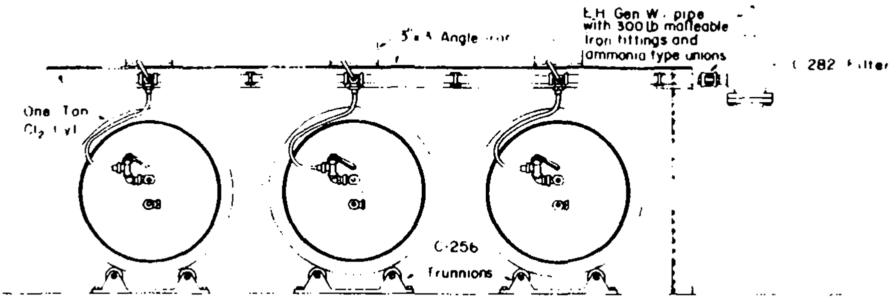

Fig 9-10 Gas withdrawal system for ton containers

as possible to the last ton container (Fig. 9-10) If the header between the last cylinder and the chlorinator is subject to temperature variations of 20°F or more over a twenty-four-hour period, then it is desirable to install an external pressure-reducing valve This valve prevents liquefaction of the chlorine in the header system and the chlorinator mechanism caused by wide variations of the ambient temperature. This valve should be installed immediately downstream from the filter shown in Fig. 9-10. This filter is a combination sedimentation trap and filter. The filter medium is spun fiber glass, which is held in place by a stainless steel insert and screen assembly

*Liquid Withdrawals.* The chlorine header system for liquid withdrawal is somewhat different from that for gas withdrawal The piping and support system are the same, except that the flexible connections to the auxiliary header valve are connected to the bottom cylinder outlet valve (the top valve is for gas withdrawal). Because of the evaporator in the system, the filter is located immediately downstream of the evaporator outlet The filter must always be installed in the gas phase It is not possible to filter out chlorine impurities in the liquid phase, because the impurities are in solution This places the filter just upstream from the chlorine pressure-reducing valve, which now becomes an automatic shut-off valve as well.*

A complete liquid withdrawal system is illustrated in Fig 9-11 which also shows proper spacing of the evaporator-chlorinator system

It is to be noted that some engineers prefer to use duplicate header systems from the containers to the evaporators In this way one header can be taken out of service for the required periodic cleaning without interruption of the entire facility Most systems rely on a single header however duplicate headers have advantages from an operator's viewpoint

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* This pressure reducing and shut off valve is always a part of the evaporator system It is electrically interlocked with the evaporator water bath temperature and automatically shuts off the chlorine supply in the event the water bath temperature falls below 150°F

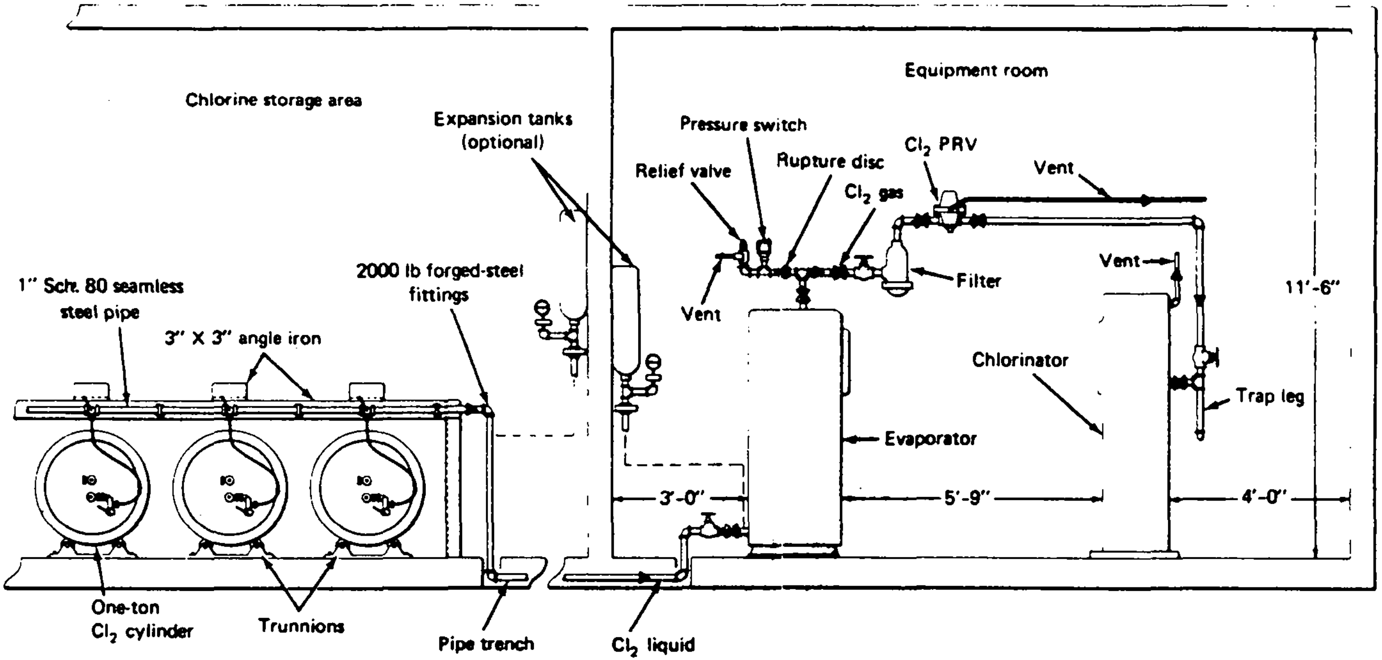

Fig. 9-11. Liquid withdrawal system showing chlorinator and evaporator spacing and ancillary equipment.

When contemplating the use of liquid withdrawal versus gas withdrawal, the following advantages of a liquid withdrawal system should be considered:

1. The danger of reliquefaction of chlorine between the containers and the chlorinator is all but eliminated.

2. Fewer cylinders need to be connected at one time. Liquid withdrawal rates of a ton cylinder can be as high as 10,000 lb/twenty-four hours.

3. The evaporators, although insulated, do give off some heat in the equipment room.

Liquid-withdrawal systems do not have the critical design problems with regard to temperature considerations as do the gas-withdrawal systems, except for inadvertent trapping of liquid in the header system which constitutes a temperature-pressure hazard. If liquid chlorine is trapped between two shut-off valves and the ambient temperature rises a few degrees, the liquid chlorine will try to expand. Since it cannot expand it will exert a pressure in accordance with the vapor pressure temperature curve shown in the Chlorine Institute Manual. For example, suppose a container connection full of liquid chlorine is trapped by yoke shut-off valves and at each end a ton container or a tank car (at an ambient temperature of 80°F) is removed, then the vapor pressure would be 100 psi. Now if the connection full of liquid were allowed to reach a temperature of 90°F by placing it in the sun, the hydrostatic pressure of the contained liquid would probably exceed the tensile strength of the already fatigued flexible connection resulting in a rupture of the flexible connection.

A note of caution about manifolding ton containers withdrawing liquid: always be sure that the temperature of the cylinders is about the same; never connect "hot" cylinders to the manifold simultaneously with cylinders already in use.

The cylinders can be placed in carport-type open structures with only a sunshield when the system is operating entirely on liquid withdrawal (Fig. 9-7). If the cylinder storage area is remote from the chlorine control system, it is desirable to install an expansion tank in the header system using a frangible disk and pressure alarm in series with the expansion tank. (See Fig. 9-12). This device is necessary to protect the system against the condition where an operator might close both the outlet valve on the header and the inlet valve to the evaporator, thereby trapping liquid in the header. Any subsequent ambient temperature rise would result in a pressure rise in the liquid chlorine sufficient to rupture the header piping. This is a direct result of the hydrostatic pressure due to the expansion of the liquid chlorine (or $SO_2$) which is greater than that of the steel pipe or copper flexible connection as a function of a rise in ambient temperature.

Since chlorine headers must be cleaned occasionally, it is desirable in most cases to install duplicate headers between the cylinder area and the chlorination equipment.

In either liquid or gas withdrawal systems using ton containers or tank cars, a sediment trap should always be provided where the gas line enters the chlorinator. Fig. 9-11 illustrates such a trap. This minor item saves much maintenance time

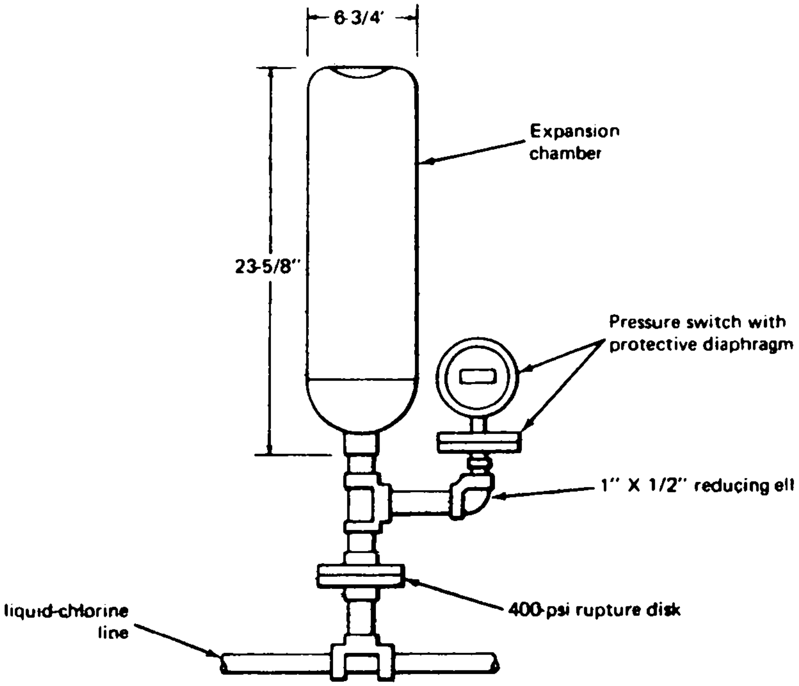

Fig. 9-12. Liquid chlorine expansion chamber. Connection is to liquid phase only. All fittings are 2000 lb CWP forged steel. All piping is seamless carbon steel Sch 80. Teflon tape should be used at all threaded joints

on chlorination equipment. The chlorine gas line nearly always enters the chlorinator from the vicinity of the ceiling. The necessary downdrop to each chlorinator is a potential collection place for chlorine sludge caused by the inherent impurities in the chlorine. These deposits are the result of the reliquefaction phenomenon. A trap 12 inches long and capped will catch most of this debris and prevent it from entering the control mechanism of the chlorinator

*Platform Scales.* These are available for weighing one or more cylinders, up to a maximum of five. They are available in dial indicating and/or dial indicating plus recording models

*Weighing Devices Using a Hydrostatic Load Cell with Remote Dial Readout.* These are popular for installations using ton cylinders. Fig. 9-13 illustrates a load cell unit for weighing one ton cylinders. This unit features a remote digital readout at a much lower cost than beam- or pipe-lever-type scales. This type of scale is also available with electronic type load cells. These systems are capable of providing a variety of chlorine inventory information.

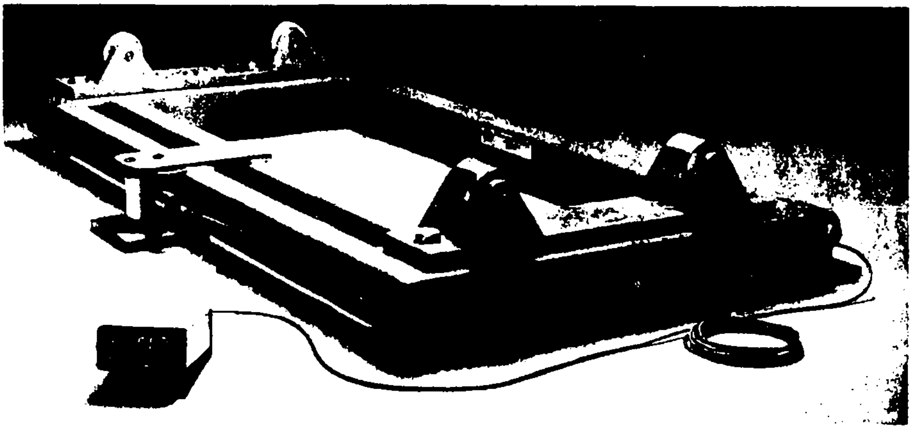

Fig. 9-13. Ton cylinder load cell type scale with digital readout (courtesy Chlorine Specialties, Inc).

*External Chlorine Pressure Reducing Valve.* Gas withdrawal systems which operate under pressure as opposed to the remote vacuum systems are subject to chlorine reliquefaction due to the ambient diurnal temperature changes. To prevent, reliquefaction, which is highly undesirable, a pressure reducing valve should be installed in the gas header. It should be located adjacent to the last cylinder in the header system. These valves are available in capacities of 500, 2000, and 10,000 lb/day.

*Chlorine Gas Filter.* Every installation using ton containers for gas withdrawal should have a chlorine gas filter as close as possible to the last cylinder, and always upstream from the external reducing valve or remote vacuum regulating valve.

*Expansion Tanks.* These tanks are necessary only when there is danger of liquid chlorine becoming trapped in the supply line. Then if there were a significant ambient temperature rise, hydrostatic pressure from the liquid chlorine trying to expand would rupture the pipe. One thing is certain, however: spring-loaded relief valves discharging to atmosphere should never be used on liquid chlorine lines. The chance of such a valve reseating properly is remote.

Figure 9-12 illustrates an expansion tank recommended by the Chlorine Institute. This tank utilizes a frangible disk that will rupture at some desired pressure between 300 and 400 psi, thereby allowing the liquid trapped in the system to enter the expansion tank.* This immediately produces some vapor pressure in the expansion tank, which actuates the pressure switch and sounds the alarm.

Systems employing long liquid lines and/or chlorine storage tanks usually have electrically operated valves at both ends of the lines. When there is a power failure

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* If for any reason the header piping is subjected to a vacuum the rupture disk will be damaged. Therefore these disks must be specified for vacuum operation on the pressure side.

or a pressure drop, these valves close. An expansion tank is required on such lines equal in volume to at least 20 percent of the line volume between the automatic valves. The chlorine pressure-reducing and shut-off valve on the discharge side of the evaporator will also close on power failure, trapping the liquid in the evaporator. This will cause an immediate pressure rise in the evaporator, since the liquid chlorine in the evaporator will tend to reach the temperature of the water in the surrounding water bath. The vapor pressure in the chlorine chamber of the evaporator will rise until there is equilibrium in the temperature gradient between the liquid chlorine and its surrounding water bath. This would be close to 160°F, which is equivalent to a vapor pressure of 315 psi.

This condition is exaggerated when two or more evaporators are manifolded together and operating at maximum capacity at the time of power failure. In such cases, the vapor pressure could reach 425 psi.

To alleviate this condition, one or more expansion tanks must be connected into the system on the liquid inlet line to each evaporator just downstream from the automatic electric shut-off valve on the liquid supply header. Fig. 9-11 illustrates the proper arrangement of an expansion tank to take care of any liquid which might get trapped in the evaporator; it also illustrates the conventional location of an expansion tank to handle any liquid which might get trapped in the supply header system.*

For installations where the supply system is close coupled to the evaporators, there is no appreciable danger from closing valves at the outlet of the supply system simultaneously with the closing of the inlet to the evaporator; therefore, expansion tanks are not required. It is also deemed necessary to provide pressure relief of the evaporator between the inlet shut-off valve and the downstream shut-off valve in some instances.

Operators should be thoroughly and properly instructed never to close valves in this system so as to trap the pressure in any part of the liquid portion. The basic rule is never to shut off the outlet of the supply container unless the system is being secured. In these instances, the pressure on the entire system is then allowed to go to zero gage pressure.

Chapter 11 outlines operating procedures for securing a liquid supply system so as to eliminate the necessity for relying on expansion tanks for those systems that do not use automatic electric shut-off valves on the liquid lines.

*Gages.* If the system is utilizing gas withdrawal and it is close coupled, gages in the chlorine gas header can be omitted, since the gage on the chlorinator will suffice. However, if this gage fails, it does not leave the operator with any means to determine whether or not the system is "live." An extra gage is always useful.

If the system utilizes an external pressure-reducing valve, there should be one gage upstream from this unit and one downstream.

For a liquid withdrawal system, the evaporator has a gage showing the system

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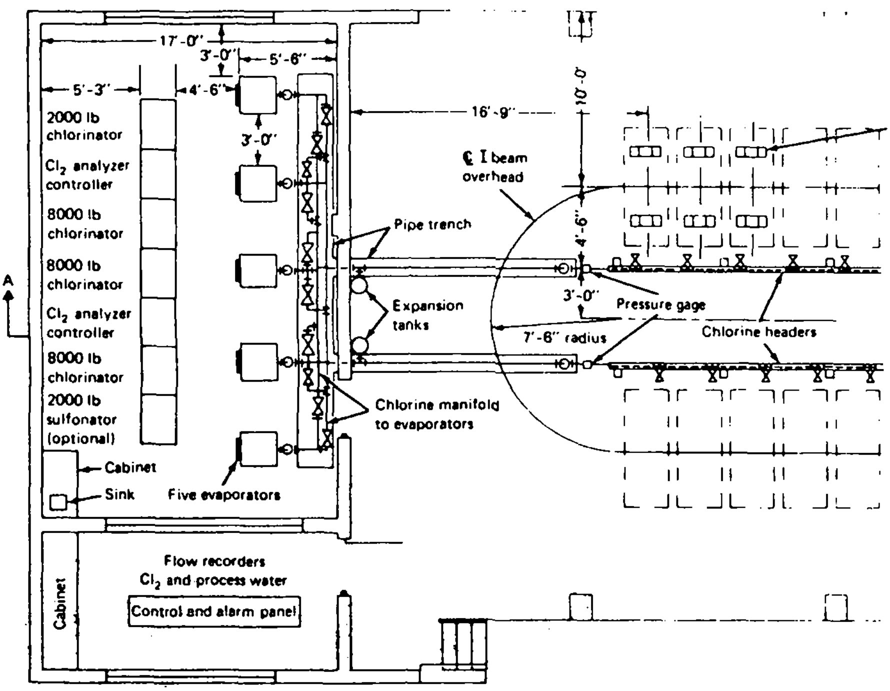
* Fig. 9-11 also illustrates the 1975 mandatory evaporator relief system (see p. 637). The expansion chamber concept is the safest because it prevents a chlorine emission.



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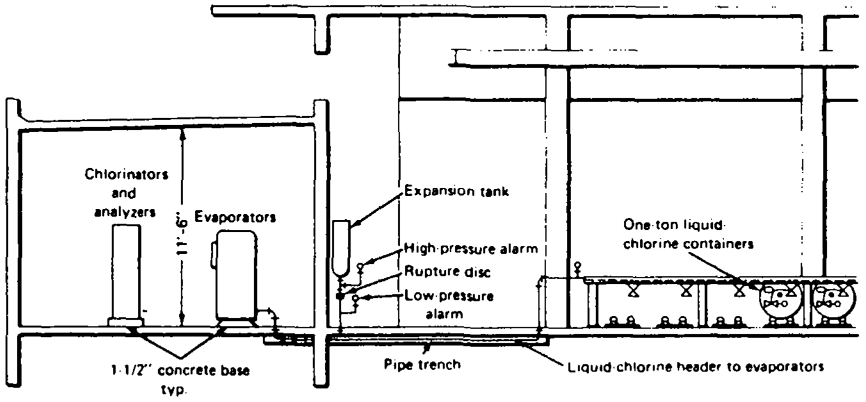
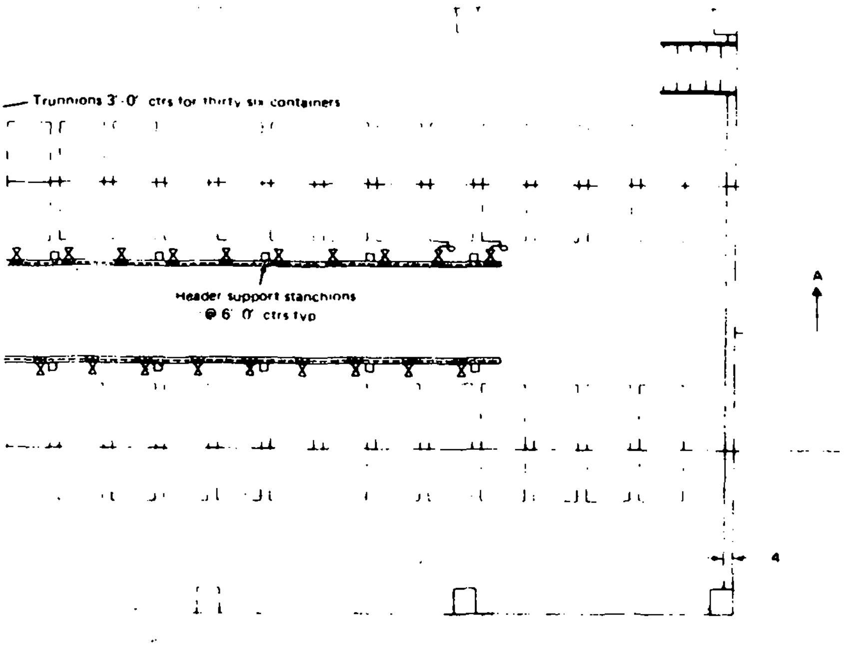


SECTION A

Fig. 9-14. Chlorine storage and handling facilities, equipment and space requirements for 24000 lb/day capacity.


Trunnions 3'-0" ctrs for thirty six containers
Header support stanchions
@ 6'-0" ctrs typ
A
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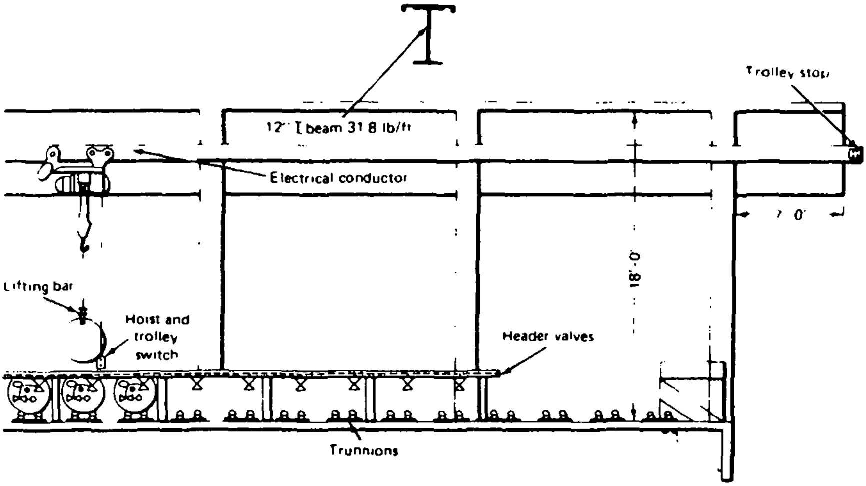
12" I beam 31.8 lb/ft
Trolley stop
Electrical conductor
7'-0"
18'-0"
Lifting bar
Hoist and trolley switch
Header valves
Trunnions

pressure. It is useful to have another gage on the liquid line between the containers and the inlet shut-off valve to the evaporator. A gage downstream from the pressure-reducing and shut-off valve should be considered, unless the system is a one-chlorinator installation that is close coupled. In the latter case, the chlorinator gage could be sufficient. However, when chlorinators and evaporators are manifolded together, it is always desirable to have gages downstream from each reducing valve. Similarly, when these systems are interconnected, it is also desirable to have gages upstream from each reducing valve. When more than one evaporator is involved, there should be a gage on the liquid chlorine inlet line to each evaporator upstream of the evaporator inlet shut-off valve and downstream from the evaporator isolating valve. These gages are extremely helpful to the operator, for safety reasons as well as for troubleshooting.

*Alarms.* Pressure switches that sound an alarm are helpful, and should be considered on most installations. Two kinds of pressure alarm devices are available. One is an adjustable mercoid type switch that has adjustable contacts which close for either rising or falling pressure; the two functions are not now available in the same housing. The other is a combination indicating gage and pressure switch. The U.S. Gauge Co. Model 3050 is adjustable to sound an alarm at both high and low pressures. Its contacts are adjustable over the entire range of the gage.

All liquid withdrawal systems should have a high-pressure alarm, located on the liquid supply header between the chlorine containers and the evaporators, which will be activated when the pressure reaches 150 psi.

Gas withdrawal systems do not need high-pressure alarms.

A low-pressure alarm is highly desirable. It warns the operator of imminent exhaustion of the chlorine supply. In some cases it can be used in lieu of weighing devices.

For example, consider that five ton containers are in service simultaneously in a chlorination system with a usage rate of 4000 lb/day. If the low-pressure alarm is set at 30 psi on the liquid supply line, there would be approximately 30 to 40 lb of chlorine in each cylinder and 30 to 40 lb in the evaporator and piping system, or a total of approximately 150 to 200 lb of chlorine remaining in the system at 30 psi. At 4000 lb/day, the usage is 167 lb/hour. Thus, when the alarm sounds, the operator has about one hour to prepare for putting another bank of cylinders in service. The situation is the same whether the withdrawal is liquid or gas.

Fig. 9-14, a typical ton container handling system for a chlorination facility with a maximum capacity of 24,000 lb/day, indicates space requirements and the arrangement of handling facilities.

## Container Withdrawal Rates[2]:

*General Discussion.* The sustained maximum chlorine withdrawal rate will vary from plant to plant, depending primarily upon the temperature surrounding the

Table 9-1 Vapor Pressure vs. Container Liquid Temperature

| *Temperature, °F* | *Chlorine* | *Sulfur Dioxide, psi* | *Ammonia* |
|---|---|---|---|
| 0 | 14 | | 16 |
| 10 | 21 | | 24 |
| 20 | 28 | 2 | 34 |
| 30 | 37 | 7 | 45 |
| 40 | 47 | 12 | 59 |
| 50 | 59 | 18 | 75 |
| 60 | 71 | 26 | 93 |
| 70 | 86 | 34 | 114 |
| 80 | 102 | 45 | 138 |
| 90 | | | |
| 100 | | | |

container, characteristics of the chlorinator installed, and the size of the container.

Chlorinators require a minimum gas pressure for proper operation, again depending upon the type of chlorinator. Most vacuum-type units require at least 10 psi but are more reliable at 15 psi inlet pressure. The gas pressure at the point of withdrawal is a function of the chlorine liquid temperature in the container. This relationship is shown in Table 9-1. The table is derived from graphs that can be found in the Appendix.

For a given chlorinator, the temperature at which the minimum required gas pressure is reached is termed the "threshold temperature." For example, Table 9-1 shows the pressure needed for a typical vacuum-operated chlorinator occurs at about 0°F (14 psi). Therefore 0°F is the threshold temperature for that type of chlorinator. The liquid chlorine in the cylinder or container must be kept at 0°F to maintain the gas pressure required for proper operation.

When gas is withdrawn from the container, the liquid in the container is chilled. To maintain the liquid at the threshold temperature, heat must pass from the air surrounding the cylinder through the walls of the container and into the liquid. Therefore the maximum sustained rate of withdrawal is directly dependent upon the rate at which this heat transfer takes place. Several factors influence the heat transfer rate, including ambient temperature, air circulation, humidity of the air, amount of liquid remaining in the container, and size and type of container. In general the important factors are: (1) ambient air temperature and (2) size and type of cylinder. Ambient air temperature is simply the air temperature surrounding the container.

*Container Withdrawal Factor* The size and construction of the cylinder can be related to the ambient temperature with a number called a "withdrawal factor." Table 9-2 lists several withdrawal factors.

Table 9-2 Withdrawal Factors

| Gas | Withdrawal Factor |
|---|---|
| Chlorine | |
| 150 lb cylinder | 1.0 |
| 1 ton container | 8.0 |
| Sulfur dioxide | |
| 150-lb cylinder | 0.75 |
| 1-ton container | 6.0 |
| Ammonia | |
| 150-lb cylinder | 0.4 |
| 250-lb cylinder | 0.8 estimated |
| 800-lb container | 3.2 estimated |

*Sample Calculation.* The equation used to calculate the maximum withdrawal rate from a container is as follows

$$\text{(Temp. of Room} - \text{Threshold Temp.)} \times \text{Withdrawal Factor}$$
$$= \text{Max. Withdrawal rate, lb/day}$$

Assume room temperature or ambient temperature surrounding the container is 70°F, the withdrawal temperature is 10°F. The withdrawal factor is 8 for a ton container. Then we have (70 − 10) × 8 = 480 lb/day. The rule of thumb is often quoted as 400 lb/day, which is a more practical figure. The example shown in the calculation would cause excessive moisture condensation on the cylinder, resulting in copious quantities of water accumulating on the floor of the container area. Visible moisture in the chlorine or chlorinator areas should be *avoided*.

## Automatic Switchover, Ton Containers:

*General Discussion.* Unattended chlorination stations must have special provisions to preclude the possibility of chlorine supply failure. Traditionally chlorine supply systems have been provided with scales for determining the amount of chlorine remaining in the connected cylinders. If this is the sole means of accounting for the chlorine supply, it requires frequent checking and operator judgment to determine when the cylinder will become empty. This diminishes facility reliability. The operator may find that he is faced with repeated interruptions in chlorination.

To solve the problem of chlorine supply reliability a great many stations have adopted the automatic switchover concept in lieu of scales. There are two types (1) the pressure system and (2) the vacuum system.

*The Pressure System.* This system has been in use since about 1966. It is illustrated in Fig. 9-15. This arrangement of pressure reducing valves, gage, valves, and piping

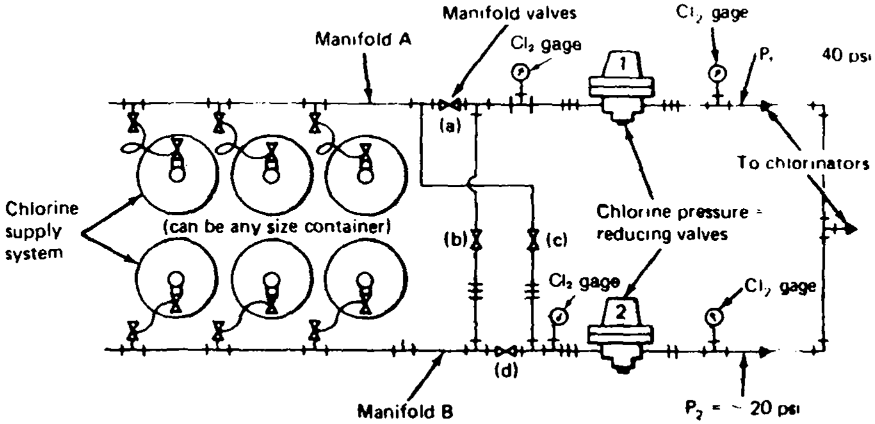

Fig. 9-15. Automatic chlorine cylinder switchover (gas phase only). By reversing manifold valves a,b,c, and d, chlorine can be routed from manifold A to CPRV #2 and manifold B to CPRV #1.

usually requires less capital outlay than required for weighing devices. Use of this system greatly improves the overall reliability of the chlorination facility

The system consists of two independent manifolds, each equipped with a manually adjusted chlorine pressure-reducing valve (CPRV) and the necessary gages CPRV-1 is set 10–20 lb higher than CPRV-2. Therefore, only gas will flow through regulator 1, and only from manifold *A*. When all the liquid chlorine in the cylinders connected to manifold *A* vaporizes, and the gas pressure drops to the set limits, CPRV-2 will open, allowing the full cylinders on manifold *B* to supply the chlorine With the higher pressure setting on CPRV-1, gas from manifold *B* cannot flow back into the cylinders connected to manifold *A*. The lower pressure reading on each gage is evidence to the operator that chlorine is now coming from manifold *B*. After the empty cylinders connected to manifold *A* have been replaced by full ones, the manual valves ahead of the regualtors are reversed so that the gas from manifold *B* now passes through CPRV-1 (higher pressure), which will again cause automatic switchover when the cylinders are empty

*The Vacuum System.* The Wallace and Tiernan version of this system utilizes the dual arrangement of the vacuum-regulator check unit used in the remote vacuum arrangement for ton containers.[3] The switchover system is illustrated in Fig. 9-16. For automatic switchover capability two vacuum regulators are fitted with mechanical detents One regulator feeds gas until the container to which it is connected is nearly exhausted. The resulting rise of vacuum to higher than normal provides sufficient force to unlatch the detent in the second regulator which then takes over the gas supply function. The original supply continues to feed with the new supply, insuring exhaustion of gas from the original supply container

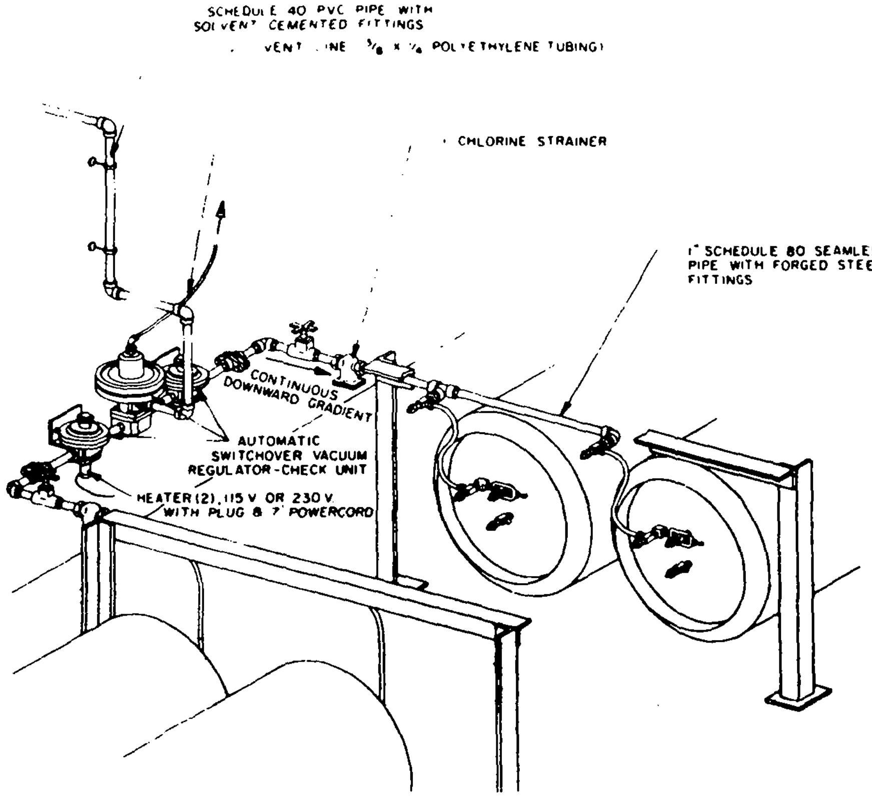

Fig. 9-16 Automatic chlorine cylinder switchover: Vacuum type, gas phase (courtesy Wallace and Tiernan Div Pennwalt Corp.).

Referring to Fig. 9-16, it is imperative that the vacuum-regulator check unit be vented to outside atmosphere well above ground level where chlorine fumes cannot cause injury to personnel or damage to foliage.* Avoid areas routinely used by personnel, near windows, recirculated or ventilation air ducts.

This automatic switchover unit remains in the closed position and will not open until a vacuum is produced on the downstream side by the chlorinator injector. The entire unit is designed to withstand full container pressure. If the first valve passes gas without a vacuum, the second valve will remain closed and contain the cylinder pressure within the unit In the extremely unlikely event that the

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* When multiple chlorinators are involved serious consideration should be given to the use of a mini-absorption tank for these and other similar vents

second valve passes gas (without a vacuum) the built in pressure relief valve will allow this gas to pass out the vent to atmosphere

*Liquid Chlorine* Automatic switchover for ton containers operating from the liquid phase is shown in Fig 9-17 The pressure switch is in the common liquid line if multiple evaporators are in use This arrangement can be used with some modification for tank cars However, the preferred method for tank cars is the reserve tank

When the pressure is on the liquid side of the evaporator it is presumed to be set at 20–25 psi This will insure that all of liquid has been exhausted and only vapor remains in the supply system The electrically operated valves in the supply line should open slowly enough to accommodate the near empty situation downstream from these shut-off valves

Another method used is a sonic liquid chlorine level sensor as used in the reserve tank system This system depends upon the operator to strip the exhausted supply system of any liquid and the remaining vapor As shown in Fig 9-18 this stripping

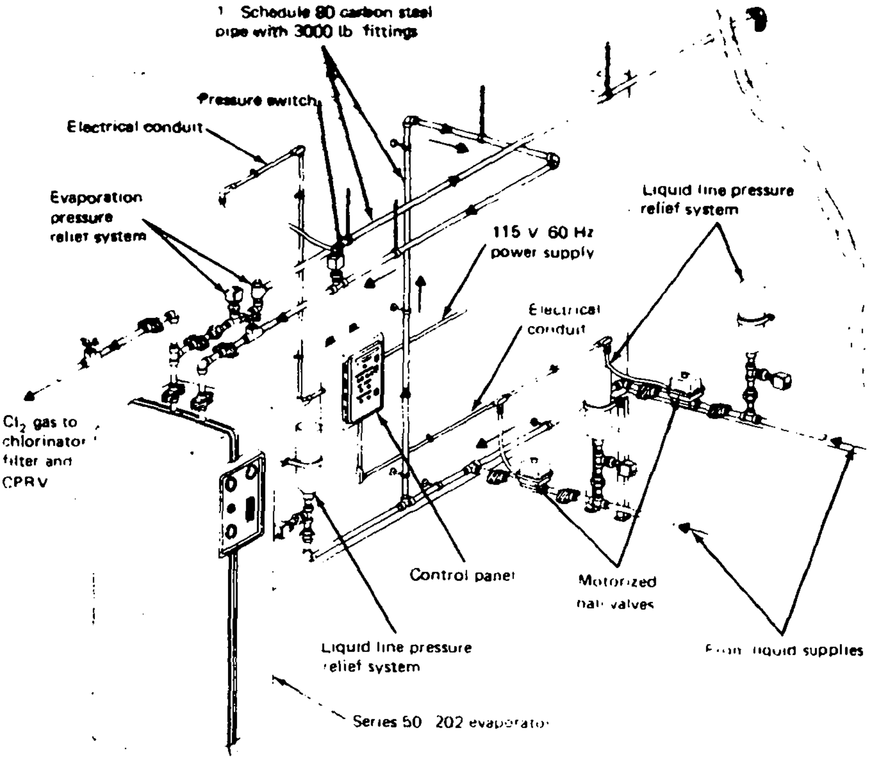

Fig 9-17 Automatic chlorine supply switchover system for liquid withdrawal (courtesy Wallace and Tiernan Div Pennwalt Corp)

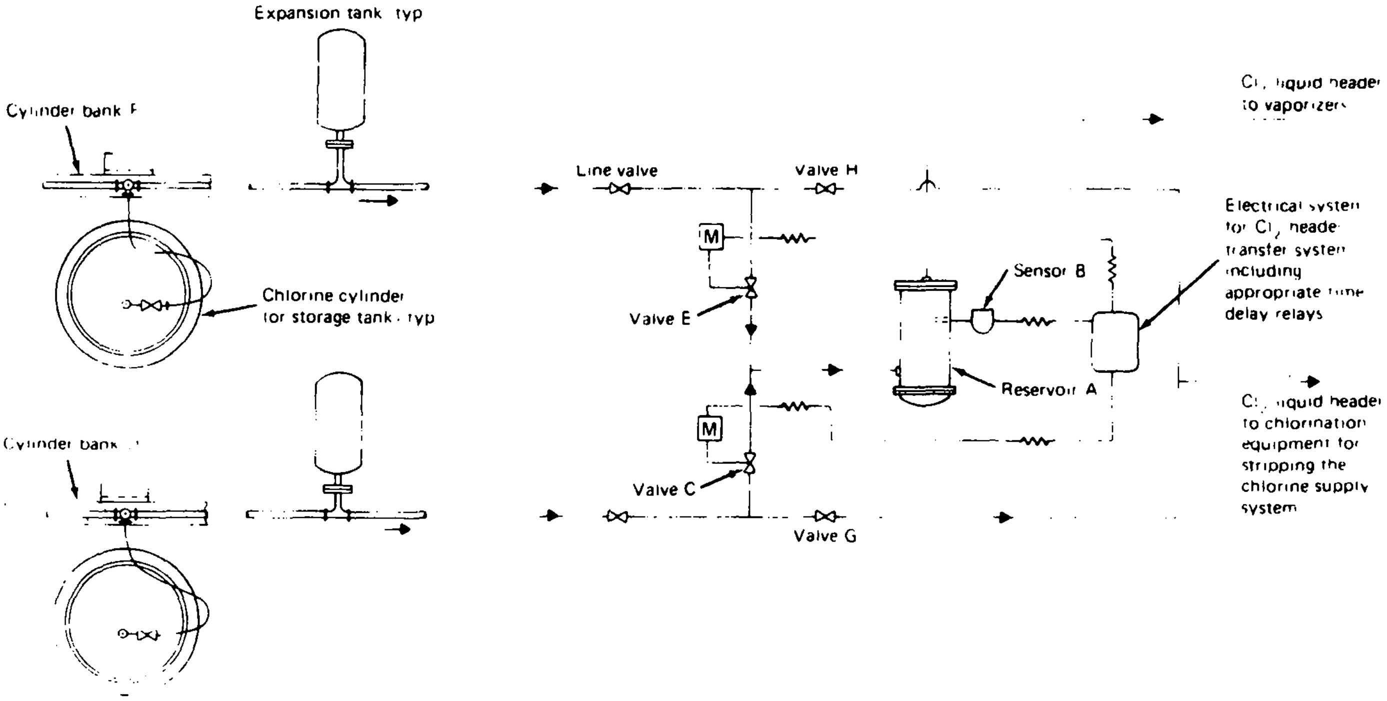

Fig 9-18 Automatic liquid chlorine supply switchover system using a sonic level sensor

line is a separate header which should be connected to the alternate top liquid connection on the evaporators.

This system has been used for many years in the pulp and paper industry

**Selection of Container Size.** The first step in the design of a chlorination facility is to decide on the size of the chlorine containers to be used. This depends primarily on the average daily consumption of chlorine. It becomes a problem of economics and logistics, although a few mitigating circumstances might take precedence over these factors, such as length of haul and accessibility to the chlorine storage area.

For the purpose of economic evaluation, the following are the relative costs of chlorine in the various size containers. These prices fluctuate considerably, depending upon the area, but will usually remain in relative ratios.

| *Size Container* | *Cents/lb $Cl_2$* |
|---|---|
| 100- to 150-lb cylinder | 15 |
| Ton containers | 7½ |
| 55 to 90 ton tank car | 3¾ |
| Storage tank | 3½ |

Another cost factor to be considered is the demurrage charge on the containers. Depending upon the chlorine packager, this may be a flat charge for any container kept longer than thirty, sixty, or ninety days, or it may be reflected in a price break for ordering multiple quantities at one time plus a demurrage charge on each container kept longer than ninety days.

Other things being equal, and considering the practical aspects of an installation, 150-lb cylinders are the containers of choice when the average daily consumption of chlorine does not exceed fifty pounds. These cylinders are readily handled by one man using a special two-wheel hand truck.

When the daily consumption is in excess of fifty pounds, ton containers are to be considered. More space must be allotted and special handling equipment must be provided for these containers.

Tank cars should be considered when the average daily consumption of chlorine reaches two tons per day, which would require a weekly delivery of fourteen ton cylinders. This is about the maximum quantity which can be handled by truck rigs for one load.

The use of a storage tank may be considered for any installation using tank cars, particularly if the average daily consumption is four tons per day or more

**Designer's Check List for Chlorine Supply System: Ton Cylinders.** The following is a guide to remind the designer to check the chlorine supply layout for all necessary accessories:

1. Cylinder weighing scales or load cells
2. Trunnions for ton containers
3. Ton cylinder lifting bar
4. Chlorine gas filter
5. External chlorine pressure-reducing valve
6. Liquid chlorine expansion tank
7. Appropriate gas and liquid supply pressure gages
8. High- and low-pressure indicating switches for alarms. (High-pressure alarm is used only on liquid systems.)
9. Condensate traps at inlet to chlorinators
10. Appropriate header valves and shut-off valves

## Single Unit Tank Cars:

*General Description.* Chlorine is available in five sizes of single-unit cars: 16, 30,[*] 55, 85, and 90 tons. Each car is equipped with an outlet dome that is made identical for all tank cars approved by the Chlorine Institute. This dome contains two liquid outlet valves that are in line with the longitudinal axis of the car and two gas outlet valves on an axis at right angles to the liquid valves. In the very center of the dome is a safety relief valve that will expel gas to atmosphere under overpressure conditions. In each liquid outlet line, there is installed a safety check valve described as an excess flow valve. In case the car is in an accident and the valves are sheared off, the check valves will jam in a shut tight position due to the momentary velocity of the liquid exiting through the sheared off valve. This is why any tank-car withdrawal system should be equipped with a rotameter to see that the unloading rate is less than that which will cause the check valve to jam closed. This rate is usually 7000 lb/hr.[**]

Tank car dimensions are shown in Table 9-3.

Figure 9-19 illustrates the pertinent features of tank car construction. These cars are provided with a cork or a combination fiber glass and foam insulation from 4 to 6 inches thick, covered with an outer steel jacket, to minimize vaporization and pressure buildup in transit.

The only opening in the tank, at the center on top of the car, is closed by the dome plate, which is sealed by a lead gasket and secured with a ring of bolts.

The mechanism for chlorine withdrawal from a tank car is shown in Fig. 9-20. Four forged steel angle valves are mounted on the cover plate which is secured to the dome, a fifth is a safety relief valve. These valves have Monel seats and stems, and are protected by a false dome with a hinged cover. Openings around the false dome, protected by close-fitting covers, permit access for connection to the valves. The two angle valves on the longitudinal axis of the car are for liquid withdrawal. An eduction pipe extends from each liquid discharge valve to the

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[*] The 16 and 30 ton cars are being phased out of service in most areas.

[**] Excess flow valve rates vary for car size.

## Table 9-3 Dimensions of Tank Cars

| | *Length Over Strikers** | *Overall Height†* | *Height to Valve Outlet†* | *Extreme Width‡* |
|---|---|---|---|---|
| TMU | 42' 4"-47' 0" | 6' 8" 7' 6" | | 9' 6" 10' 1" |
| 16-Ton | 32' 2"-33' 3" | 10' 5" 12' 0" | 9' 3¼"-10' 0' | 9' 2 9' 6½' |
| 30-Ton | 33' 10"-35' 11½" | 12' 4½" 13' 7" | 11' 3" 11' 9" | 9' 3" 9' 10" |
| 55-Ton | 29' 9"-43' 0" | 14' 3' 15' 1" | 12' 6" 13' 4" | 9' 3" 10' 7½" |
| 85-Ton | 43' 7"-50' 0" | 14' 11" 15' 1" | 13' 2" 13' 4" | 10' 5½" 10' 6½" |
| 90-Ton | 45' 8"-47' 2" | 14' 11" 15' 1" | 13' 2" 13' 4" | 10' 5½" 10' 6½" |

* Add 2' 6" for length over center line of coupler knuckles

† Heights are for empty cars, and are measured from top of rail. Heights for loaded cars may be 4" less

‡ Width over grab irons

*Note:* Height to manway platform is 6 to 10' less than height to center line of valve

bottom of the car. Just beneath each of these valves in the eduction pipe are excess flow valves, as shown in Fig. 9-21. These protective devices are designed to close automatically in case of a major break in the angle valve or in the chlorine unloading pipeline. These valves seat only when the clorine flow reaches approximately 7000 lb/hour. This flow rate shut-ff varies with car size.

For the layout of a single-unit car unloading site, the designer should consult the *Chlorine Institute Manual*[1] which quotes from the ICC regulations for chlorine unloading.

A dead-end siding should be provided for chlorine unloading. Tracks should be level. The car should be protected by a locked derail at least one car length away from the end of a car hooked up for unloading. If the car must be on an open siding, both ends should be protected. If a switch is involved, it should have a lock; the keys for the switch and the derail should only be in the hands of the person responsible for unloading.

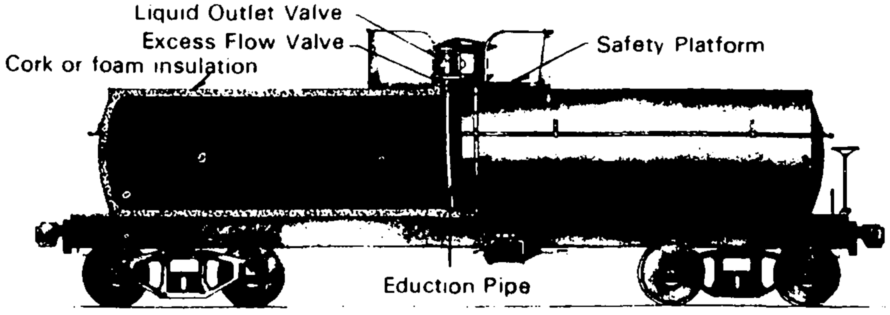

Fig. 9-19 Single unit chlorine tank car (courtesy PPG Industries Chemical Division)

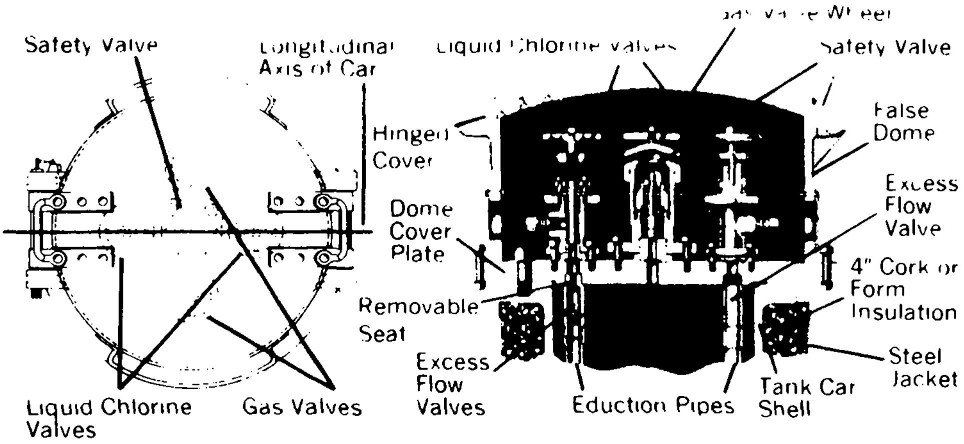

Fig 9-20 Chlorine tank car dome (courtesy PPG Industries, Chemical Division)

An operating platform must be provided at the unloading point to provide easy access to the dome for connecting and disconnecting the loading lines and for operation of the valves. This platform should be of such height that it is suitable for working on cars of any of the sizes listed in Table 9-3

*Flexible Connections.* Two types of flexible connections for use between the car dome and the piping system are available the annealed copper loop, and the flexible

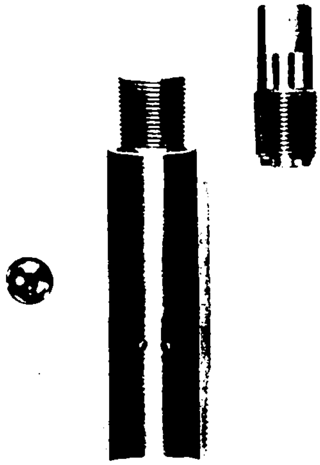

Fig. 9-21 Tank car excess flow valve (courtesy PPG Industries, Chemical Division)

reinforced metal hose The connections are fitted with 2-bolt ammonia-type unions with a lead gasket joint It is customary and desirable to connect a pressure gage to one of the gas valves on the car dome. An L-shaped pipe assembly is used to permit mounting the gage where it can be seen from the unloading platform

One flexible connection is used to join one of the liquid withdrawal valves to the liquid header piping, and the other is used to connect one of the gas withdrawal valves to the air padding system This gas connection can also be used to connect the gas withdrawal valve to the gas header piping.

Flexible connections should be plugged at both ends with corks immediately upon removal from the tank car and stored in a heated compartment This minimizes corrosion and extends the active life of the flexible connections.

*Header System.* Two completely separate headers are required between the tank car (or storage tank) and the evaporators: one for liquid and one for gas. It is at times necessary to withdraw gas from the supply system. In the event of a leak in the tank car discharge system or header piping the ability to withdraw gas can be used to reduce the tank car pressure. Accordingly, a field test was made with a 55-ton car approximately half full at the beginning of the test[4] Three 8000-lb chlorinators operating simultaneously were used for this test. Withdrawal of approximately 2030 lb of chlorine reduced the car pressure from 98 psi to 37 psi in 3¾ hours. Ambient temperature was 55°F. The pressure drop caused a liquid chlorine cooling effect of 47°F. This represents 43 lb liquid chlorine per degree F drop. However, from 37 psi to 20 psi required only 30 min and 208 lb of chlorine to produce and additional cooling of 24°F, or 9 lb chlorine per degree F

The presence of two header systems is also desirable for standby service Tank car consumers using a duplicate header system have reported frequent use of the second or standby header for routine maintenance. Each of these headers should be equipped with a pressure gage immediately downstream from the shut-off valve on the unloading platform.

*Air Padding System.* This is required for unloading the tank car and for pressurizing cars in cold climates. Chlorine is usually shipped cold. Assuming a median temperature of 40°F, the vapor pressure will be 45 psig. Use only clean dry air free of oil and foreign matter. Air must be dried to at least a -40°F dewpoint measured at atmospheric pressure.

The air padding system should incorporate the following elements.

1. Oil-free air compressor with after-cooler and receiver
2. Air dryer
3. Air filter (oil absorber type)
4. Dewpoint indicator
5. Dewpoint alarm
6. Vapor pressure alarm system

## Table 9-4 Tank Car Capacity

| | *55-ton Car* | *90-ton Car* |
|---|---|---|
| Water capacity, gal | 10564 | 17298 |
| Total car volume, ft$^3$ | 1410 | 2335 |
| Liquid $Cl_2$ volume 60°F, ft$^3$ | 1240 | 2035 |
| Gas volume space, ft$^3$ | 170 | 300 |

Table 9-4 itemizes the volume characteristics of a 55 ton and 90 ton car.

Table 9-5 gives the amount of padding air required to pressurize a 55-ton and a 90-ton car to various pressures.

The air flow required to unload a tank car at a given rate can be calculated by the following formula:

$$\frac{\text{SCFM Air} = \text{lb/day Chlorine} \times (P_{car} - 25)}{1.8 \times 10^6} \tag{9-1}$$

Selection of an oil-free air compressor is the objective of a reliable air padding system. An example is the Corken Pump Co. of Oklahoma City, OK. Any selected compressor should be supplemented with a Deltech filter for compressed air. The compressor should be equipped with an ASME code receiver of appropriate size with an air-cooled after-cooler mounted on the receiver.

Suitable air dryers are available from Deltech Engineering Co., Century Park, Newcastle, DE 19720 and Lectrodryer, Box 4599, Pittsburgh, PA 15205. The air dryer can be the heat reactivated type capable of operating up to 150 psi. The air flow capacity of the dryer should be 1.5 times the compressor capacity discharging at a maximum dewpoint of -40°F. This part of the system should be equipped with a dewpoint indicator and a high humidity alarm.

A critical part of the air padding system is the check valve which prevents chlorine vapor from entering the system. Installations using ordinary ball check valves have invariably suffered from chlorine vapor getting into the air pad system. Spring-loaded check valves have proved to be somewhat more reliable, but they too have caused corrosion problems.$^5$

## Table 9-5 Dry Air Required to Pressurize Tank Car*

| | *Volume of Free Air (ft$^3$) Required to Achieve Car Pressure Shown (PSI)* | | | | | |
|---|---|---|---|---|---|---|
| *Car Size* | *60* | *75* | *90* | *105* | *120* | *135* |
| 55-ton car | 170 | 340 | 510 | 680 | 850 | 1020 |
| 90-ton car | 300 | 600 | 900 | 1200 | 1500 | 1800 |

* Assume median liquid $Cl_2$ temp 40 F and car pressure 45 psig

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* This is the only instance where a check valve is optional in the chlorine supply system. Check valves at other locations (flex connections, header piping, etc.) should never be used. In a chlorine atmosphere they are unreliable due to corrosion products. Moreover they would be hazardous to operating personnel.

The Chlorine Institute Pamphlet No 4. "Consumer Air Padding of Chlorine Single Unit Tank Cars," illustrates a power operated shut-off valve instead of a check valve This is the preferred method Fig. 9-22 illustrates a power operated shut-off valve system used for many years by the Pennwalt Corporation, Tacoma, WA [6]

Each air padding system should have its own separate and independent air supply When both chlorine and sulfur dioxide are present the air padding system must never be used interchangeably Each liquid-gas supply must have its own air-padding system

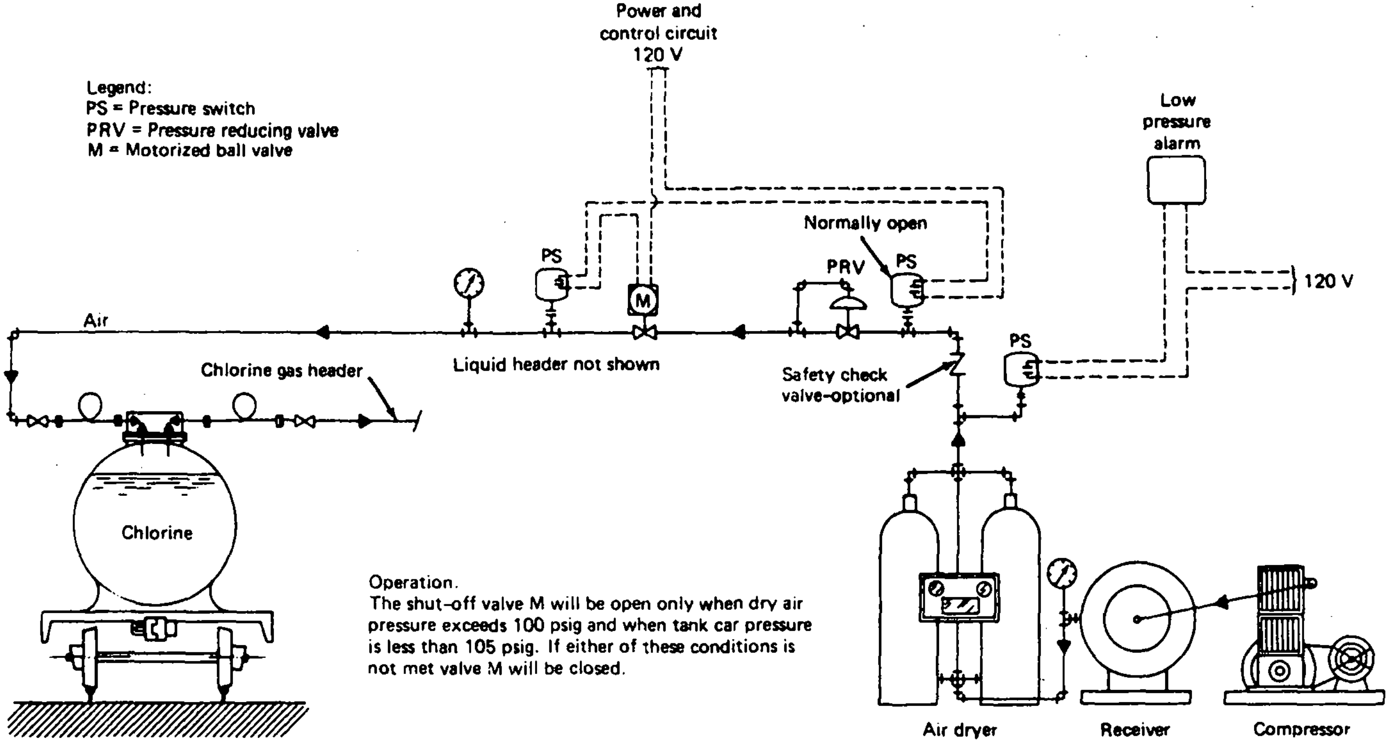
Whenever air padding is deemed unnecessary, then nitrogen purging facilities should be considered mandatory This consists of a sufficient number of nitrogen cylinders which contain nitrogen gas at 2000 psi and a common pressure regulator with an outlet pressure regulated at 150 psi. This system should be arranged to allow the operator to purge the entire header system back into the containers. This system is most advantageous in the handling of liquid chlorine.

*Absorption Tanks.* In addition to purging and air padding systems, tank-car systems should be provided with a liquid chlorine absorption tank. This tank should be able to absorb all the liquid chlorine in the header piping and evaporators. The absorption tank should be made of reinforced Fiberglas or rubber-lined steel. It should have a vent, a special connection for caustic, and one for makeup water. There should also be a sampling tap to determine the effective absorption capacity of the solution. The piping of the liquid chlorine to the tank must have a barometric loop (see reserve tank system). The downdrop of this loop and the sparger (diffuser) should be made of Kynar pipe. The size of the absorption tank is based upon the stoichiometric combination of caustic (NaOH) and chlorine which is 1.13 lb of caustic for 1.0 lb chlorine. The absorption tank must have a minimum depth of 8 ft and the caustic solution is usually kept between 0.5 to 1.0 lb/gal.

EXAMPLE. 1000 lb chlorine requires 1130 lb caustic for neutralization. One gallon of 50 percent caustic contains 6.38 lb caustic. Therefore 1130/6.38 = 177 gal of 50 percent caustic is required for each charge of the absorption tank to neutralize 1000 lb of liquid chlorine. So to provide a tank having about 1.0 lb/gal caustic, the absorption tank should have a capacity of approximately 1200 gal

## A PLAN TO DEAL WITH A MAJOR CHLORINE LEAK

**Definition of a Major Leak.** How to deal successfully with a major leak is a formidable task The two most discussed events are a direct hit by an aircraft and or a planned act of sabotage. The latter is usually dismissed on the basis that proper security measures can provide the necessary deterrence. The air crash scenario is usually dismissed as an improbability. However an air crash accompanied



Legend:
PS = Pressure switch
PRV = Pressure reducing valve
M = Motorized ball valve

Operation.
The shut-off valve M will be open only when dry air pressure exceeds 100 psig and when tank car pressure is less than 105 psig. If either of these conditions is not met valve M will be closed.

Fig. 9-22. Power operated shut-off valve, air padding system.

by exploding fuel results in the following consequences The aircraft impact or subsequent explosion would probably rupture the chlorine container(s) The ensuing fire would instantly vaporize the liquid chlorine and the chlorine vapor would rise quickly with the heat of the fire This sequence of events would serve to greatly diminish or eliminate chlorine exposure in the surrounding area This was clearly demonstrated when a freight train derailment severely damaged a 90-ton chlorine tank car The car was ruptured by the couplers from an adjoining butane tanker All 90 tons of chlorine were released The butane tank car exploded and all of its contents were consumed by fire The heat from this fire vaporized the liquid chlorine which disappeared into the upper atmosphere due to the rising hot air from the butane fire A subsequent investigation revealed that no one in the surrounding area or at the scene of the accident was found who had experienced any exposure to chlorine (See Ch 1).

The consensus definition of the most probable major leak is a guillotine break in the liquid chlorine header between the chlorine supply system and the chlorine evaporators. The only safe and practical way to deal with this kind of a leak is to contain it in the room and neutralize released chlorine on the spot

**Containment with Controlled Release to Outside Air.** It is assumed that the liquid chlorine header will break in the chlorinator-evaporator room and the spill will amount to no more than 2000 lb. of liquid chlorine. This would comprise the contents of all the header piping and evaporators.*

To dispose of or neutralize this amount of chlorine safely, the room where the spill occurs must be able to contain the chlorine vapor The normal ventilation system must automatically close as soon as a leak is detected This will prevent any chlorine release to the outside air

In a containment situation where the room is filled with chlorine it should be noted that a Chemtrec Emergency Response team will not enter any confined area to secure a leak until the chlorine concentration has diminished to a level compatible with breathing apparatus capability

Therefore to neutralize a major leak it is imperative to install a chlorine neutralizing scrubbing system described below

**Leak Scenario.** The 1 in liquid chlorine header to a multiple evaporator installation breaks and releases 2000 lb of liquid chlorine Ambient temperature is 80°F and liquid line pressure is 90 psi at the time of the break This will put two one inch orifices into action. one from the supply side and the other from the evaporators (back flow). Under the conditions described liquid chlorine will flow at approx 0.43 ft.$^3$/sec from each orifice This amounts to 0.43 × 2 × 88 lb/ft$^3$ = 75.68 lb/sec However a liquid chlorine leak is not that simple At the moment of pipe rupture about 20 percent of the 2000 lb of liquid will flash to vapor (400 lb)

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* Assume each evaporator will spill 125 lb of chlorine This would be a worst case operating condition

and the room temperature will drop about 30°F or 50°F This event will consume about 5-6 seconds leaving 1600 lb (approx 18 $ft^3$) which will spill on the floor in the next 20-22 seconds

If the floor space between the 40 ft long wall and the evaporators has a grated trough (gutter) and if the floor is sloped properly the remaining liquid can be captured in a confined space This arrangement will diminish the vaporization rate of the remaining liquid chlorine The liquid chlorine collection trough should be about 1 ft deep and 6 inches wide to minimize surface area According to Howerton[81] the chlorine in the trough will vaporize at a rate of 15 to 20 lb/hr/$ft^2$ The above dimensions provide a 20 $ft^2$ surface area so the remaining liquid chlorine will require about 4–5 hours to vaporize Vaporization will be intermittent because of the cyclic action of the chlorine going from stages of freezing to thawing This vaporization is dependent upon how long it takes for the ambient temperature to be restored in the chlorinator-evaporator room Therefore the total time involved to neutralize the leak described above may take up to 5 hours

## Scrubber System:

*System Description.* The venturi-ejector fume scrubber is the method of choice for a major leak. This is the method used by modern-day chlorine/caustic plants to neutralize chlorine releases during plant upset conditions.[82] A typical system is shown in Fig. 9-23

Typically a scrubber is designed to recirculate the room air until all of the chlorine spill has been absorbed by the continuous passage of room air through a caustic* solution The air recirculating rate should be sufficient to provide one complete room air turnover every two minutes The scrubber system depends upon a chlorine detector to close the normal ventilation system and to activate the scrubber blower The room air is then diverted to the scrubber suction where it travels to the inlet of the venturi throat Simultaneously with the blower activation the caustic recirculating pump starts and delivers caustic solution to the inlet of the venturi The room air is mixed with the caustic solution in the throat of the injector This is similar to a chlorinator injector operation The air flow travels through the entire vertical distance of the caustic tank and discharges to the mist eliminator The scrubbed air is then returned to the chlorinator-evaporator room

*Theory of Operation* The caustic tank is sized to hold a sufficient quantity of 7 percent sodium hydroxide to convert the chlorine gas leak to sodium hypochlorite The rule of thumb for absorption towers is 1 0 lb/gal of caustic The stoichiometric combination of NaOH and chlorine is 1 13 lb caustic per lb of chlorine Therefore a 2000 lb chlorine leak would require a theoretical 2260 lb of caustic This translates to a 2260 gallon caustic tank However the scrubber manufacturers recommend a 3600 gallon caustic tank for a 2000 lb spill[83] This factor of safety is necessary to allow for dead spaces in the tank since mechanical mixers are not practical

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* Sulfite should not be considered as a substitute for caustic Molecular chlorine will depress the pH of the solution which will release a cloud of $SO_2$ vapor

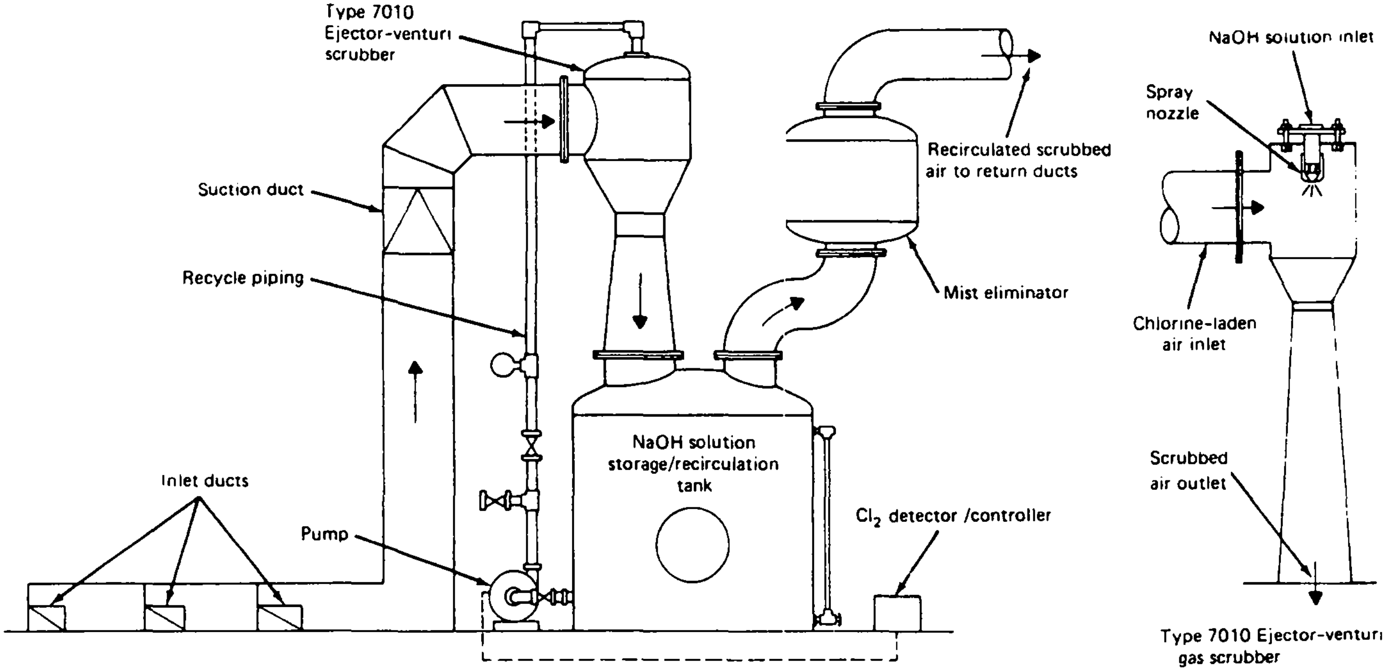

Fig. 9-23. Chlorine scrubber system (courtesy Ametek-Schutte and Koerting Div., Durham, N.C.)

The scrubber operates until the chlorine concentration in the room air is reduced to 1 ppm. Either or both the room air and caustic solution can be monitored during the scrubbing period. Instrumentation is included with the system to provide shutoff of the scrubber and reactivation of the normal room ventilation system

*Reliability.* This system has a long history of reliability because it is not dependent upon the solubility of chlorine in water due to the caustic recirculating system nor is it dependent upon scrubbing water as in wet scrubbers. If the leak is greater than expected additional caustic can be added to displace the caustic converted to hypochlorite.

*Cost.* The equipment required for a 2000 lb. leak as described above is approximately $35,000. For a lesser leak; 1000 lb. the capital cost would be about $25,000.

**Spent Caustic Disposal.** The spent caustic will be a sodium hypochlorite solution about 7000 mg/L. This is easily disposed of at a water or wastewater plant provided it can be metered in small quantities over a given period of time. The hypochlorite can be easily destroyed by catalytic decomposition using nickel and iron as catalysts.* The use of sulfites to dechlorinate the hypochlorite solution is not recommended. The heat of reaction between the sulfite ion and hypochlorite is far too great at these concentrations.

## Chlorine Tank Car Supply Monitoring Systems

*General Discussion.* Single-unit tank cars pose a problem in determining when exhaustion of the liquid chlorine is imminent. Reliance on pressure drop is not the total answer, and where air padding is used on a continuous basis (cold climate), temperature drop monitoring is not reliable. Track scales are the only direct means, but these constitute an exorbitant expense, about $50,000 to $75,000. Scales for storage tanks are much less expensive (about $5,000).

A convenient method for solving the supply monitoring problem would be to meter the flow of liquid chlorine exiting the car. Unless the car is padded to a pressure of 175–200 psi it is not possible to measure with any accuracy the flow of liquid chlorine due to its physical characteristics. As the liquid flows past a point of slight pressure drop, as in a flow meter, the liquid flashes to vapor causing a large change in density. This makes calibration of a flow meter practically impossible. *A magnetic flow meter will not respond to liquid chlorine.*

Tank cars are well insulated so that they maintain vapor pressure equilibrium until all of the liquid has been discharged.

> EXAMPLE. A 90-ton car displays a vapor pressure of 70 psi. When all the liquid is gone there will remain in the car approx. 2500 lb of chlorine gas provided

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* If available seawater will destroy the hypochlorite solution in a few hours owing to the presence of heavy metal ions.

the car has not been air padded during use This is a significant amount of chlorine that should be used by the consumer

*Chlorine Pressure Switch.* A chlorine pressure switch installed in the liquid header immediately upstream from the evaporators can be used for monitoring or automatic switchover service. A pressure switch set to alarm at 20 psi will advise the operator that approximately 1050 lb of chlorine is left in the car This may be sufficient time to switch to a new car The other alternative would be to set the pressure switch to 20 psi and use the alarm circuit to activate the motorized valves in an automatic switchover system The time between the occurrences described above is totally dependent upon withdrawal rate and to some extent upon ambient temperature Therefore a reliable and accurate pressure switch is essential for liquid chlorine supply monitoring. The US Gauge Co. Model 3050 is a combination indicating gage and pressure switch with adjustable contacts for both high and low pressures over the entire range of the gage, 0–160 psi.

*Three Detection Methods for Liquid Chlorine Exhaustion.* The liquid chlorine exhaustion point has been detected in three ways: (1) A cylindrical vessel has been used which is mounted vertically and equipped with a liquid level sensor which alarms when the level falls some predetermined distance in the cylinder. (2) All of the chlorinators have been equipped with chlorine flow recorders and a totalizer that will alarm at 500 or 1000 lb chlorine remaining. (3) The liquid chlorine temperature has been continuously monitored adjacent to the point where the flexible connection to the tank car joins the liquid header. As the liquid chlorine approaches the point of exhaustion it attempts to vaporize as it exits the tank car This premature vaporization causes a sudden drop in the temperature of the liquid as it enters the header piping at the unloading platform A temperature sensor equipped with an alarm will notify the operator of imminent liquid exhaustion. The reliability of these methods is dependent upon the withdrawal rates of liquid chlorine at the moment of exhaustion

**Reserve Tank for Liquid Chlorine Supply.** A system used for more than half a century in the pulp and paper industry is the reserve tank concept. This system was developed by the late Brian Shera of Pennwalt Corp., formerly Pennsylvania Salt Co., Tacoma, WA

This is a liquid chlorine flow-through tank, as shown in Fig. 9-24 which provides an active reserve when the car has been emptied of liquid. The tank may also be installed vertically if preferred. These tanks have been made in sizes from 1000 to 16,000 lb of chlorine. The capacity should provide approximately 1–3 hr reserve of chlorine at peak demand. Liquid chlorine enters and leaves the tank through pipes extending to the bottom of the tank. Venting of gas is necessary to provide a minimum of 20 percent gas volume as a safety factor against excessive filling of the vessel with liquid. This is accomplished by a dip pipe of an appropriate

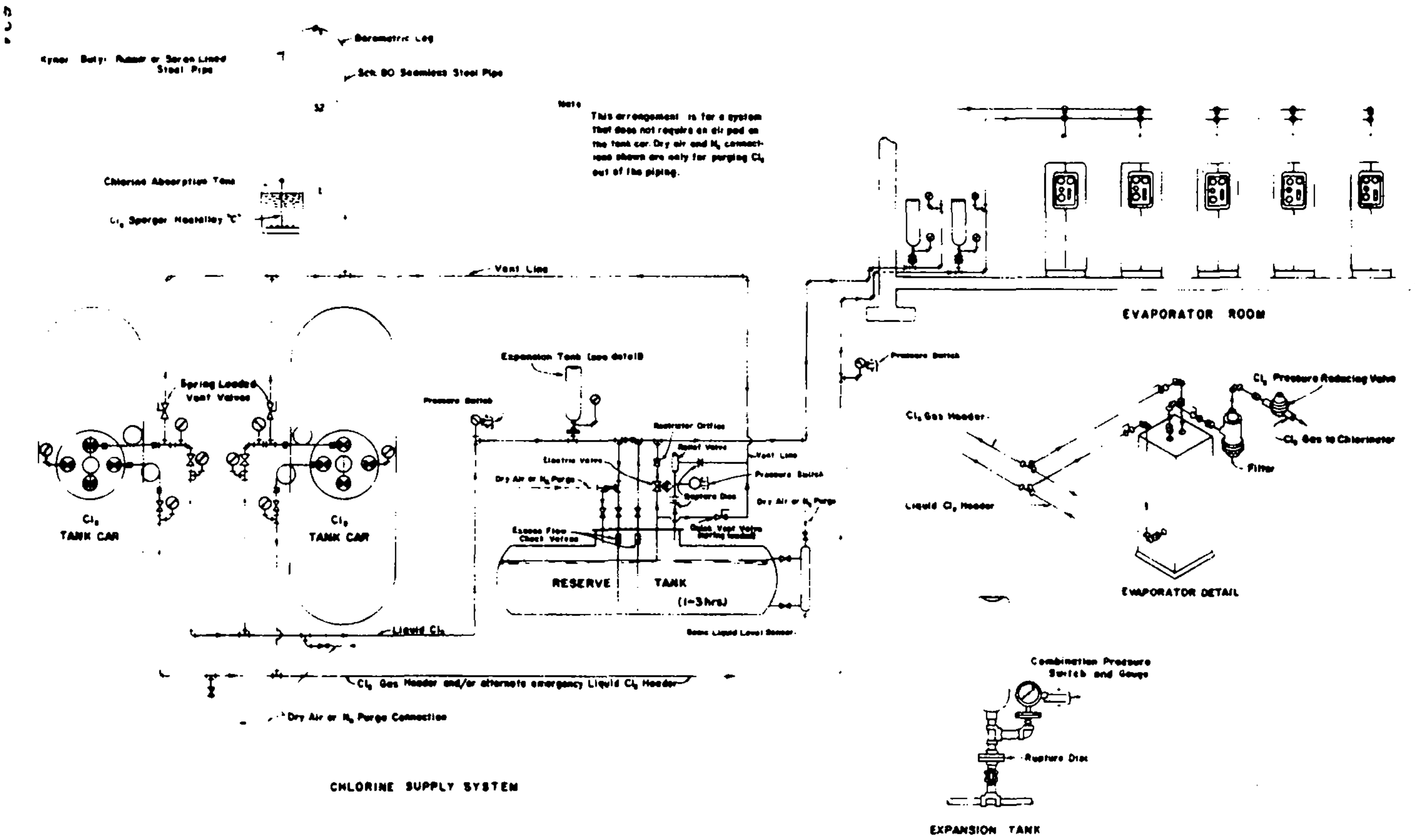

Fig. 9-24 Reserve tank system for chlorine supply system

length to provide the gas volume The vent piping is fitted with an electric shutoff valve and a restrictor orifice. Upon leaving the restrictor orifice the vent pipe joins the liquid lines going to the vaporizers. This restrictor orifice allows a minor flow of gas that will flashover from the small amount of liquid being bled from the tank thus keeping the liquid level constant in the reserve tank so long as chlorine is flowing from the tank car This vent also allows the liquid level to rise to its normal height when the reserve tank is being filled. When the liquid chlorine flow from the tank terminates, the chlorine level in the reserve tank will drop and this will be detected by the ultrasonic level sensor. The sensor sends a signal through a control box which will engage an alarm and also close the electric shutoff valve in the vent line. The operator now has two choices: shutoff the liquid flow from the reserve tank and bleed the remaining gas in the tank car to the process; or immediately switch to a full car When the time comes to switch to a new car, the reset button on the electric valve is actuated so as to open the vent line and allow refilling of the reserve tank. The reserve-tank piping and valving accessories are equipped with both automatic and manual pressure relieving devices all discharging to the absorption tank. This prevents any overpressuring of the reserve tank. The pressure relief line has a rupture disc followed by a pressure switch alarm. This is followed by a spring loaded relief valve protected from moisture entry by a rupture disc which is installed backwards for ruptures at low pressure. In addition, there is a spring-loaded manual quick vent valve to the absorption tank. Fig. 9-24 illustrates all of the appropriate expansion tanks and pressure switches required to give the operator the necessary operating information.

The following are the recommendations of the Chlorine Institute for chlorine storage tanks as set forth in Pamphlet No. 5, "Facilities and Operating Procedures for Chlorine Storage," 2nd Ed., Jan. 18, 1962.

- Minimum design volume, 25.6 $ft^3$ for each 2000 lb of chlorine to be stored
- Minimum working pressure, 225 psig plus ⅛-in corrosion allowance
- Design and fabrication, compliance with the ASME-UPV Code, 300°F, 70 percent weld efficiency, spot X-ray or 100 percent X-ray longitudinal and circumferential seams
- Nozzle necks, Sch 160, seamless steel pipe
- Piping, Sch 80 seamless steel
- Flanges, 300 lb weld-neck, slip-on, or screwed
- Fittings, buttweld extra heavy
- Fittings, screwed, 3000 lb
- Valves, 300 lb, flanged, forged steel body
- Valves, 300 lb, screwed, forged steel body

The purge connections shown are essential for the inspection and repair of the system They also prevent the emission of chlorine to the atmosphere and the entrance of moisture to the piping and tank system, thus accelerating corrosion and deteriorating the entire system This is the only way to provide a completely closed *system which prevents penetration of atmospheric moisture*

## Fully Automatic Tank Car Valve Shut-off System. (CVA)*:

*Historical Background.* The Clorox Co. of California spent several years and large sums of money developing this valve shut-off system- only for tank cars.[85] The Clorox Company has a nationwide operation of producing sodium hypochlorite from chlorine in tank cars. They have a great many of these installations in the U.S.A. In 1979 they experienced a serious leak at their Oakland, California plant. The leak occurred after a full tank car had been connected. A small leak developed in a 2 bolt flange near the car valve. The operator tried to stop the leak by tightening the bolts without shutting the car valve. As he tightened one bolt, the nut was stripped off the other bolt, partially opening the flange. This caused a significant leak of liquid chlorine. However, the size of the leak was not sufficient to activate the excess flow valve in the tank car. The leak required evacuation of people working in the immediate area and the rerouting of traffic on a heavily traveled freeway. This incident motivated the Clorox Company to seek a permanent solution to this type of problem, hence the development of this unique emergency tank car security system. It is probably the most significant contribution towards safety in chlorine handling in the last 50 years. This system incorporates the latest technology in mechanical, electrical and instrumentation engineering. Reliability of the system has been established by rigorous and lengthy field testing and operation.

*System Description.* Three separate components make up the entire system. They are: a DC motor operated valve actuator, an instrument control module and leak detector units.

The motor operated valve actuator is the heart of the system. It is a unified piece of machinery which is shaped to fit inside the circular tank car dome. The actuator fits over the tank car outlet valve so that there is no need to make any modifications or adjustments of the tank car valve. The gear train operated by the DC motor is designed to exert a 50 ft-lb torque on the valve stem. The torque is designed to be self limiting which prevents the actuator from shearing the valve stem or damaging the valve in any other manner.

In addition to the valve actuator the Clorox Company developed a Chlorine Detector Logic Panel (CDLP) to increase the sensitivity and reliability of the chlorine leak detector. The CDLP electronic package incorporates the logic to *close the valve only.* Closing time is 18 seconds. The tank car valve must be opened manually using a handwheel attachment on the top of the CVA.

The CVA will close under the following conditions:

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* Car valve actuator

1. Chlorine detection by Fischer & Porter Detectachlor
2. Manual chlorine alarm
3. Manual or automatic fire alarm
4. Low air pressure
5. 120V power failure
6. Low battery power
7. Disconnected service cord to CVA
8. Manual trip at the Chlorine Detector Logic Panel or at CVA.

Power failure will not impair the system owing to the separate self contained DC power source which is under continuous recharge. Unfortunately this valve shut-off system is not available commercially at this time.

## Stationary Storage:

*General Discussion.* The use of stationary chlorine storage at both water and wastewater treatment plants has become popular due to the increased availability of bulk chlorine deliveries by truck. Fig. 9-25 illustrates a semi-trailer chlorine tank which is a part of the chlorine tanker fleet operated by the Metropolitan Water District of Southern California, Los Angeles. These trailers are loaded with chorine at the Stauffer Chemical Co. plant located at Henderson, Nevada (near Las Vegas). They are hauled some 300 miles to various treatment plants in the

Fig. 9-25. Chlorine semi-trailer tanker (courtesy Metropolitan Water District of Southern California).

Los Angeles Basin area. This practice began in the early 1960s. The chlorine tank illustrated in Fig. 9-25 has a capacity of 17 tons. Newer trailers have a capacity of 19 tons. The trailers are off-loaded into 25-ton storage tanks. These chlorine tank trailers are made by the Evans Tank Car Co. of Lubbock, Texas. General American Transportation Corporation of Chicago and American Car and Foundry (ACF Industries) of New York also make chlorine tank trailers of equivalent capacity.

*Unloading System.* When the decision has been made to utilize a storage tank to be loaded from either a tank car or tank truck a special unloading system has to be designed. A typical storage tank and tank-car unloading system is shown in Figs. 9-26 and 9-27. The essential features are:

1. Unloading platform
2. Storage tank and sun shield
3. Weighing device
4. Air padding system
5. Eductor

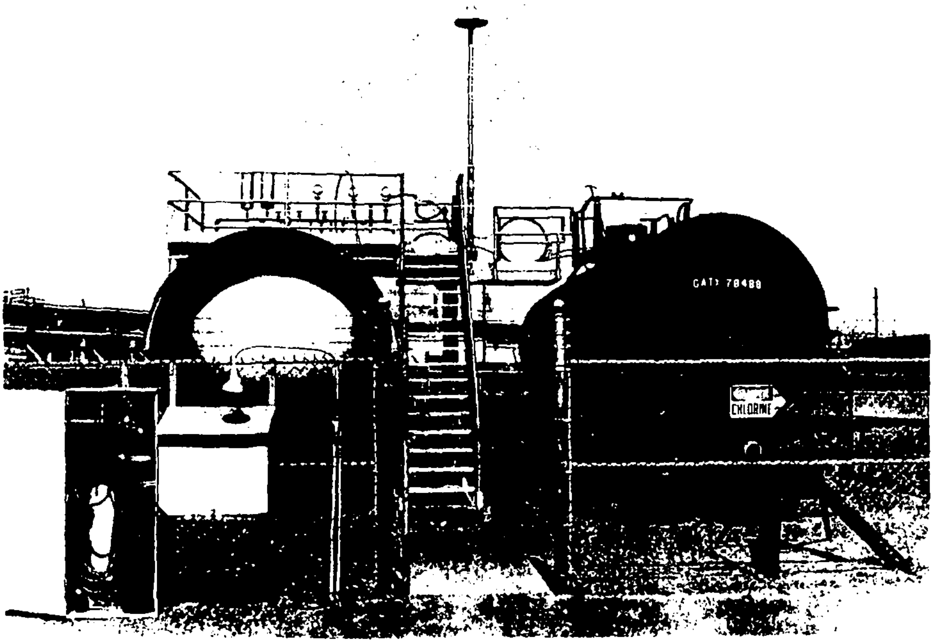

Fig. 9-26. Typical stationary chlorine storage system (courtesy East Bay Municipal Utility District).

6. Chlorine gas and liquid headers
7. Gages
8. Pressure switches and alarms
9. Expansion tanks
10. Flexible connections

The storage tank capacity for truck tankers usually is 25 tons, but the storage tank capacity for cars should be commensurate with the size of tank cars likely to be delivered. Cars usually have a capacity of 55 or 90 tons of liquid chlorine. The volume of liquid chlorine increases considerably with increasing temperature. Therefore, to provide adequate room for this expansion, the Chlorine Institute recommends that the weight of chlorine in a tank must never exceed 125 percent of the weight of water at 60°F that the tank will hold. On this basis, each ton of chlorine will require 192.2 US gallons of tank capacity.

The storage tank should be designed in accordance with the Chlorine Institute recommendations, as set forth in their pamphlet No. 5, "Facilities and Operating Procedures for Chlorine Storage." Tanks should be designed for 120 percent of the maximum expected working pressure, or not less than 225 psi. To allow for

Fig. 9-[illegible] Typical stationary chlorine storage system (courtesy East Bay Municipal Utility District)

corrosion, the wall must be 1/8 inch thicker than required by the design formula code.

The tank should be designed so that it can accept a tank car dome assembly This consists of the four outlet valves, safety valve, eductor tubes with excess flow valves, and cover assembly. It is best to purchase this entire assembly from one of the chlorine tank car manufacturers, such as American Car and Foundry, Union Tank Car Company, or General American Transportation Company

*Weighing Device.* This is imperative. Weighing can best be accomplished by the use of either a lever scale system or load cells. These systems cost about the same, but the load cell is more popular since it lends itself to remote readout and/or recording using a 4–20 mA output signal.

*Air Padding System.* This requirement is mandatory for stationary tanks. It is used for both tank car unloading (transfer) and process. It is necessary for purging the tank to allow inspection. For details see "Single Unit Tank Cars" in this chapter.

*Ejector System.* Some kind of system must be provided to evacuate the tank for both inspection and repairs. This can best be accomplished by using a standard 2" chlorinator injector. The inlet of this aspirator type of injector is connected to a supply of water at about 50 psi. The throat of the injector (suction side) is connected to the gas withdrawal line on the tank.

*Piping and Header System.* Fig. 9-28 illustrates a typical piping system for a chlorine storage system. It is important to point out the necessity of two header systems: one for gas withdrawal, and one for liquid withdrawal Both of these enter the chlorination system at the liquid inlet side of the evaporator. Gages should be provided as shown.

The flexible connections from the tank car to the tank may be of either annealed copper tubing or flexible metal hose.

Copper tubing, with a two-foot diameter expansion loop and silver-soldered copper nipples on each end, has been the most widely used. On each end an ammonia type union is threaded onto the copper nipple.

In recent years flexible metal hose has been available and seems well suited to this application. It should be made of corrugated Monel with Monel wire braid and Monel nipples that are helium arc welded to the hose The ammonia unions are threaded to each end. The total length of these flexible connections need be only ten feet.

Expansion tanks, equivalent to 20 percent of the header volume, should be used between the storage tank and the inlet to the evaporator

As an added precaution to prevent overfilling of the tank in the event of a failure in the weighing system, dip tubes can be threaded into the dome section

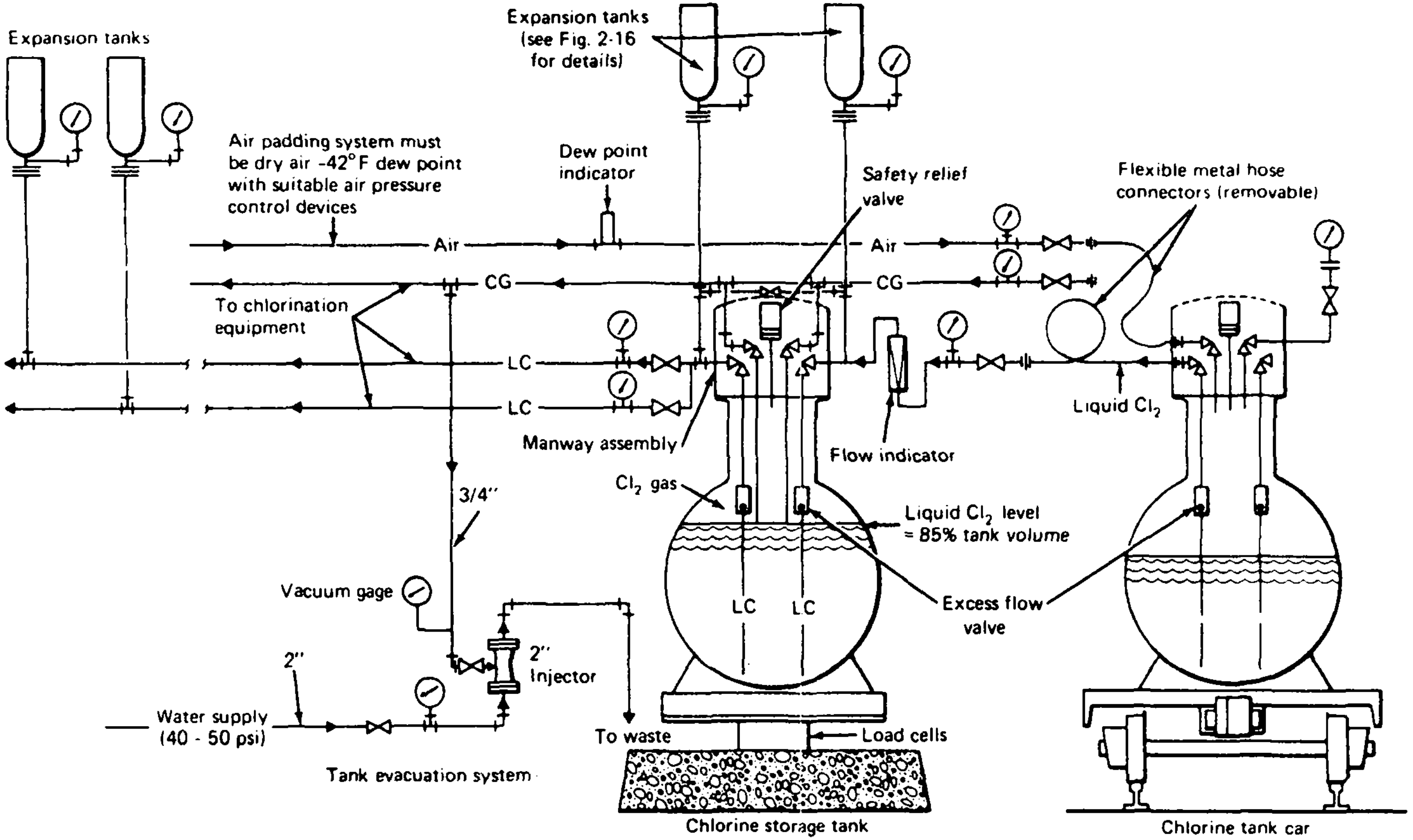

Fig. 9-28. Bulk chlorine storage and tank car unloading system. LC refers to liquid chlorine; CG refers to chlorine gas. The liquid chlorine header is in duplicate. A separate gas header is provided so that any car that arrives with too high a pressure (>125 psi) may be relieved to a lower pressure. (Dip tubes must extend far enough into the tank so that liquid contents cannot exceed 85% of the total tank volume.)

just under each gas outlet valve. Fig. 9-28 shows how these tubes come into operation. The storage tank is being filled from the tank car via line *L*. Gas is being withdrawn to the chlorination system via line *G*, which joins the chlorine liquid line at the evaporator. Whenever the tank is filled "too full," liquid will be discharged through line *G* to the evaporators. The operator will immediately notice the cooling in line *G*, signifying that the liquid transferred from the car has reached the bottom of the dip tubes. The operator should then stop the unloading process.

The length of the tubes can be arbitrarily calculated on the basis of the maximum ambient temperature to be expected in the vicinity of the tank. For example, at 100°F the liquid chlorine of a "full" tank would occupy 92 percent of the volume. This corresponds to 85 percent at 70°F, which is the recommendation of the Chlorine Institute. The depth of liquid to fill 92 percent of the tank can be calculated. The distance from the liquid to the inlet of the gas withdrawal valve determines the length of the dip tubes.

In some areas of the United States and Canada, chlorine is available in tank trucks (Fig. 9-29). It is usually imperative that the user transfer the contents of the truck to a storage tank rather than tie up the truck for the length of time of consumption of the contents. Storage tanks for tank truck operations follow the same design requirements as those loaded from tank cars, except for size. The capacity of most tank trucks ranges from 15 to 20 tons. Thus, the storage tank capacity need not usually exceed 25 tons. Depending on the length of haul and his chlorine consumption, the user should consider duplicate tanks.

## Materials of Construction:

*Chemical Reactions.* Liquid chlorine is always packaged in steel containers. Liquid chlorine which is absolutely free of moisture will not react with iron or steel

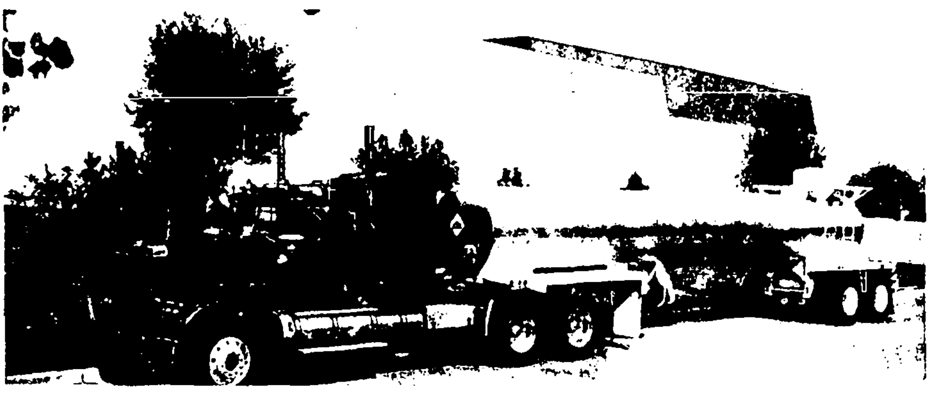

Fig. 9-29 Bulk chlorine tank truck (courtesy Evans Tank Co. Lubbock, Texas).

which is similarly free of moisture. From a practical standpoint, it is not possible to package chlorine free of moisture; therefore a very small amount of ferric chloride develops in each container of chlorine. This moisture is unavoidable because there is always some moisture in the atmosphere and because containers are cleaned by being flushed with water. Although packagers are meticulous about drying the containers after flushing, first with steam and then with hot, dry air, enough moisture still remains to form some ferric chloride, a corrosion product of chlorine and iron or steel. This corrosion process is very slow. The design of containers and pipe lines should provide extra wall thickness to take care of this factor.

The two most significant chemical reactions of liquid chlorine and the materials of construction are:

1. Liquid chlorine* will spontaneously ignite and support combustion of carbon steel at 483°F (See Chapter 1.)
2. It will attack and dissolve PVC at ambient temperatures.

The lessons to be learned here are:

1. Never apply heat directly to a chlorine container. An infrared lamp applied to the liquid portion of the cylinder can cause the burning of a hole through a steel cylinder.
2. Never use PVC or simiiar plastic materials anywhere in the liquid chlorine system or anywhere where chlorine gas is under pressure that is related to the vapor phase of the liquid–gas supply system. This usually means between the chlorine containers and the inlet pressure-reducing valve of the chlorinator.

*Supply System.* The chlorine supply system should consist of steel and cast iron products. The *supply system* is defined as that part of the system that begins at the chlorine containers and terminates at the inlet to the chlorinator.** From the chlorinator and beyond, the materials of construction are entirely different and are discussed elsewhere.

The supply system piping must be Sch 80 black seamless steel and fittings must be 2000 lb forged steel. *Do not use bushings* (they cannot meet the 2000 lb criterion). Use reducing fittings instead.

All unions should be ammonia-type with a lead gasket joint. *Never use a ground joint union.* Filter bodies and reducing valve bodies are usually cast iron. Expansion tanks should be of welded steel construction, but can be a standard 100- or 150-lb chlorine cylinder. Valves for the chlorine supply system should be Chlorine Institute approved. Two types of valves are used, one is for main line shutoff purposes and the other for isolating cylinders (header valves). Header valves are

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* Chlorine cannot be in the liquid phase at 483°F

** There is an exception when the remote vacuum system is used. PVC pipe and fittings may be used downstream from the vacuum regulator identical to the outlet valves of ton containers, bronze bodies with monel seat and stem. Main line valves can be either the ball-type or rising stem-type. The ball-type is more popular because it utilizes a lever which not only indicates at a glance the position of the valve, but also makes it easier to operate the valve.

All gauges on the supply system must be equipped with a protector diaphragm. The diaphragm should be of silver and the diaphragm housing can be either Hastelloy "C" or silver cladded steel. Shutoff valves should not be used ahead of gauges. Gauges require a minimum of maintenance so that when replacement is needed the entire supply line should be drained of pressure before replacing or removing the gauge. The value of a shutoff valve for this purpose is lost, because a valve in a chlorine supply system loses its reliability if it is not operated on a frequent basis.

In assembling the piping system, either welded or threaded construction can be used; welded is preferable. If threaded construction is used, the contractor must be cautioned to use sharp dies and all threaded pipe must be cleaned with solvent before assembly. Pipe dope should not be allowed; instead use teflon tape for thread lubricant.

*Valves Liquid and Gas Service.* Valves on the chlorine supply side of the installation should be approved by the Chlorine Institute. The auxiliary header and container valves are identical to cylinder valves—but without fusible plugs—of bronze bodies with Monel stems and seats. Line valves are of the ball type or the rising stem type. The ball type is more popular, as it uses a handle indicating immediately whether the valve is in the open or closed position. The valves are of steel body with Teflon seat and Monel ball.

*Construction.* Extreme care must be taken during the fabrication of the chlorine supply system. Sharp dies must be used to cut the threads, and all joints must be cleaned of oil, dirt, and debris before assembly. The most satisfactory thread compound is Teflon tape; litharge and glycerine are usually detrimental to the quality of the pipe work.

For that portion of the system using PVC pipe, socket weld joints should be installed where possible. Every thread cut on a piece of PVC represents a potential weakness in this spot, since apparently adverse internal stresses are created during the thread cutting process. Threaded joints will crack at the threads if subjected to even mild vibration or shock. The older the joint, the weaker it gets.

## Evaporators:

*General Discussion.* When the rate of chlorine withdrawal exceeds 1500 lb/day an evaporator should be installed. This changes the supply system to liquid withdrawal, which has different characteristics than gas-withdrawal systems.

Evaporators are available in capacities from 400 lb/day to 10000 lb/day. In a pinch, one cylinder can discharge liquid to an evaporator at a rate as high as 12,000 lb/day. This means that an evaporator can be used to conserve space for cylinder storage if necessary. The optimum storage requirements should be based upon the quantity-discount price break that is offered by the local chlorine supplier This usually occurs at a quantity of five, thus dictating space for five in service, five empties, and a vacant space for the incoming five, or a total space for fifteen cylinders.

*Electric Heater Type.* The most widely used evaporator is the electric heater type. These are available from Capital Controls, Fischer and Porter, and Wallace and Tiernan Div. of Pennwalt. These units are equipped with G.E Calrod heating elements of various sizes depending upon the vaporization requirement It takes approximately 65,000 Btu to vaporize 8000 lb of chlorine. However, the evaporator must have a wide margin of safety to allow for the partial filling of the chlorine vessel with impurities inherent in the manufacture of chlorine. Therefore, to provide a sufficient safety factor, the chlorine gas which is vaporized must contain at least 20°F of superheat to prevent misting or liquid chlorine fallout in the gas discharge piping.

Misting occurs when the evaporator is pushed beyond its capacity. This is detrimental to the chlorinator because the little globules of mist contain the various impurities inherent in the production of chlorine. These impurities will plate out at the various stages of pressure reduction. This is another reason why a chlorine gas filter should always be installed immediately downstream from the evaporator The important details to examine when comparing evaporators are as follows: volume of chlorine container vessel (extra volume is required for inherent sludge deposits); surface area in contact with water bath; volume of vapor space as determined by depth of penetration of gas discharge pipe into the container vessel; magnitude of hydrostatic pressure test; and allowable working pressure

*Beatty's Mixture.* For more than 15 years the Metropolitan Water District of Southern California has been using a liquid mixture of water and corrosion inhibitor instead of a continuous flow of fresh water for the evaporator water bath. The mixture consists of 1 pint of closed-system corrosion inhibitor No. B-239 to 10 gallons of demineralized water. Each 8000 lb/day evaporator installation is supplied with 5 gallons of this solution. Operators add the solutions to the evaporator water bath on a biweekly basis from the 5 gallon containers. In 1982 MWD reported[7] that use of this fluid for evaporator heating has eliminated scaling problems with immersion heaters, and has eliminated the need for cathodic protection of water bath and chlorine container vessels.

*Hot Water Type.* Evaporators are also available for use with recirculated hot water. One type utilizes the intermittent recirculating flow of hot water pumped in a circuit between a heat exchanger and the evaporator water bath A temperature probe actuates the recirculating pump to maintain the water bath between 170 and 180°F In another hot water arrangement, a treatment plant utilizes a closed-loop hot water system, in which water at 200°F is intermittently pumped through a coil in the evaporator hot water bath at approximately 10 gpm. This arrangement requires an independent water bath makeup system.

*Steam Type.* Vaporizers are available that use live steam instead of recirculated hot water These units are available from Whitlock Mfg. Co. in capacities as high as 5000 lb/hr of chlorine. Custom-made evaporators are also available from specialty manufacturers in Seattle, Washington and Toronto, Canada. These vaporizers can be furnished for either steam or water heated by a special propane-fueled heater *

*Chlorine Pressure Reducing and Automatic Shutoff Valve.*** Integral with the evaporator is the electrically interlocked chlorine pressure shutoff valve on the discharge line of the evaporator. The circuit that operates this valve, whether an air solenoid for a pneumatically operated valve or an electric motor operator, is connected to the low-temperature alarm circuit. The alarm circuit sounds and deenergizes the CPRV circuit when the water bath temperature drops to 150°F. This protects the chlorinator against possibly receiving severely damaging liquid chlorine from the evaporator.

*Cathodic Protection and Insulation.* All evaporators using a water bath should be equipped with a cathodic protection system to protect both the water bath tank and the outside of the chlorine container from aggressive water corrosion. This system is provided with an indicating ammeter on the evaporator instrument panel to verify cathodic protection.

The outside of the water bath should be insulated with a ½-inch covering of urethane foam.

*Accessories.* Accessories that are consistent with good practice and should be standard equipment but which are still considered by the manufacturers as optional are a gas temperature gage and automatic water level control of the water bath. Standard accessories include a gas pressure gage, water level indicator, and low-temperature alarm switch. A high-temperature alarm switch is optional.

*Electrical Requirements: Electric Heater Type.* 1 A three-wire 240 or 480 V circuit for the heater elements in the evaporator water bath. The load requirement is 12 kW for 6000 lb/day and 18 kW for 8000 lb/day.

2 A two-wire 120 V circuit is needed for the following functions:

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* The Metropolitan Water District of Southern California uses one of these evaporators as part of their 30000 lb/day mobile chlorination system

**This valve is an imperative for remote vacuum systems

a Air solenoid or electric operator on chlorine pressure reducing and shutoff valve downstream from the evaporator, interlocked with low temperature alarm
b Low temperature alarm
c High-temperature alarm (optional)
d Solenoid valve to makeup line to water bath
e Water level pressure switch

3 Alarms for each evaporator should include low temperature of the water bath, and low water bath level

## Evaporator Pressure Relief System:

*Historical Background.* Until as recently as 1974 there was no mandatory requirement to provide any pressure relief device for the liquid chlorine vessel in an evaporator. However, the manufacturers of chlorine evaporators have always been conscious of the possibility of liquid vessel ruptures. The prevailing belief was and still is that any pressure relief system creates more of a hazard than it might prevent. Therefore, evaporators have always been designed with enough strength to hold any vapor pressure that could conceivably be encountered. Furthermore, the overall system design mitigates against any possibility that might allow the liquid vessel to get "skin" full of liquid chlorine. As a final precaution, the classic design of an evaporator is to have the connections to the liquid vessel made with lead gasketed "ammonia-type" unions. These unions act like relief valves under extremely high pressures. However, since the liquid chlorine vessel is fabricated according to the ASME Boiler and Pressure Vessel Code, it is subject to rigid inspection regardless of who the manufacturer may be and must therefore be certified accordingly.

As of December 1975,[7] all pressure vessels manufactured in accordance with Division 1 Section VIII of the ASME code must be protected from overpressuring by means of a safety device. This safety device need not be provided by the vessel manufacturer, but must be provided prior to placing the vessel in service. This latest code defines the general requirements of pressure relief devices. The relief valve must be able to relieve the pressure in the liquid chlorine vessel when this pressure exceeds 110 percent of the rated working pressure of the vessel.

The Chlorine Institute specifies in Pamphlet No 9 that chlorine vaporizing equipment must have a pressure relief device.[9] This can be either a rupture disc or a spring loaded relief valve or both, preferably discharging to an adsorption system. When both are used the section between should be equipped with a vent or pressure alarm.

The State of California safety orders for "Unfired Pressure Vessels" indicates that in addition to compliance with the ASME Code the following control is also required

467 Controls: (a) Any pressure vessel not specifically covered or exempted elsewhere in these orders shall be protected by one or more safety valves or rupture discs set to open at not more than the allowable working pressure of the vessel* and by such other controlling and indicating devices as are necessary to insure safe operation.

*Current Practice.* Both Fischer and Porter[10] and Wallace and Tiernan, Div. of Pennwalt Corp.[11] provide as optional equipment a relief valve system for all their various types of evaporators. Both illustrate the location of the relief valve on the gas and *not the liquid* phase of the evaporator connections. This current arrangement is shown in Fig. 9-30. It should be noted that all rupture disks can be damaged if subjected to a vacuum. They must be specified to withstand 25 in. Hg vacuum on the pressure side.

*Relief Valves.* The Fischer and Porter relief valve Model 71P1412 has been manufactured for over 20 yr. This valve opens at about 275 psig and seats tightly at about 200 psig. Fischer and Porter report a high-confidence level for this valve.

The Wallace and Tiernan valve carries Part No. U25470. It opens at 560 psig and closes at 550 psig. This valve is purchased from Crosby Valve Co. and other suppliers such as Dresser Industries and Ferris Valve Co.[12]

*Safety Considerations.* The discharge of the relief valve system (vent) brings up serious questions about the hazards of chlorine leaking to the atmosphere at high pressures. Whenever either of these valves open to relieve pressure they become subject to atmospheric corrosion. Maintenance routine should therefore require that the valve be overhauled after each opening or closing cycle. Moreover, this valve must be protected at all times from chlorine vapor by installing a rupture disc as recommended by the manufacturer (upstream from the valve). This keeps the valve clean and dry during the periods of nonuse.

Owing to the potential hazard of a chlorine leak it is always advisable but not mandatory to discharge the vent from this system into a chlorine absorption tank. Therefore, all of these systems should be designed so that at a later date a barometric loop and absorption tank can be conveniently added to the relief valve vent. (See section describing "Reserve Tank.")

*Absorption Tank for Relief Valve Vent System.*** In addition to a suitable size absorption tank (containing NaOH), the discharge piping between the relief valve discharge and the absorption tank must contain a barometric loop. (See Fig. 9-24). The barometric loop is mandatory with an absorption tank because it prevents the almost certain intrusion of moisture into the chlorine gas supply piping.

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* Both Fischer and Porter and Wallace and Tiernan use a working pressure design of approximately 500 psi at 212°F and a hydrostatic pressure test of 1450 psi at 125°F.[12,13]

** This tank should also be considered for remote vacuum regulator vents and external CPRV vents.

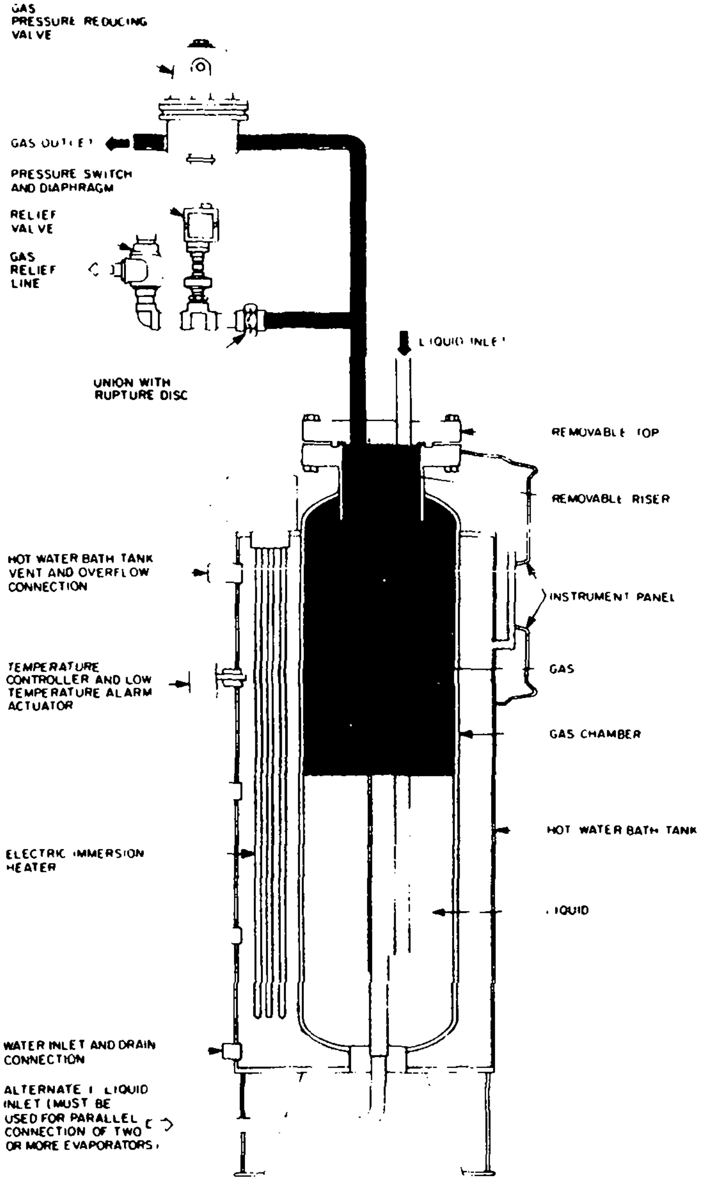

Fig 9.30 Evaporator showing relief system (courtesy Wallace and Tiernan Div Pennwalt Corp.)

The absorption tank should be capable of neutralizing a maximum of 150 lb liquid chlorine from each evaporator during an overpressure crisis situation. This is about the amount of liquid chlorine which would be contained in each evaporator if the liquid vessel were full of liquid chlorine. While this is an improbable situation it provides a generous safety factor to the size of the absorption system. To this amount of chlorine should be added the amount in the liquid piping and expansion tanks* between the supply tanks and the evaporators.

*Monitoring Relief System.* As shown in Fig. 9-30 there will be a pressure switch to monitor a critical overpressure situation sufficient to rupture the frangible disk. However, it is recommended that if this relief system is vented to the atmosphere and not to an absorption chamber the vent should be combined (but separated) in such a way that this vent and the usual chlorinator and chlorine pressure reducing valve vents be monitored continuously by a chlorine leak detector.

## SAFETY EQUIPMENT AND ACCESSORIES

**Breathing Apparatus.** There are two types of breathing apparatus, the canister-type gas mask and the oxygen or air-type breathing unit. The canister-type gas mask is limited in effectiveness; it is appropriate for changing chlorine cylinders or normal maintenance work. It is not satisfactory for use in repairing a leak. Therefore, either of the following types of equipment should be furnished: the air-type breathing unit (with 30-minute air supply, as manufactured by Mine Safety Appliance Company or Scott Aviation Company) or the oxygen breathing apparatus (as manufactured by MSA). The latter is similar to a canister type. When the seal on the unit is broken, the unit manufactures its own oxygen which lasts for 45 minutes. These canisters must be discarded after the seal is broken.

**Chlorine Container Emergency Kits.** Every chlorination station should have at least one chlorine container emergency kit. These kits are available for 150-lb cylinders, ton containers, tank cars, tanker trucks, and stationary storage tanks. These kits are available from Chlorine Specialties Inc., San Francisco, CA and Indian Springs Mfg. Co., Baldwinsville, NY. The kits are designed to seal off a leaking fusible plug, a leaking outlet valve, a tank car relief valve, or a moderate-size rupture in the container shell. Emergency Kit C for tank cars, tanker trucks and storage tanks** is illustrated in Fig. 9-31. Kit A is for 150 lb cylinders and Kit B is for ton containers.

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* It is reasonable to expect that the rupture discs on the expansion tanks might also be overpressured at the same time.

** Provided the storage tanks and trucks are fitted with a Chlorine Institute tank car dome assembly.

Fig. 9-31 Ton container emergency kit (courtesy Chlorine Institute N.Y. and Chlorine Specialties San Francisco)

## Leak Detectors:

*General Discussion* There are two categories of leak detectors: (1) continuous monitors of the working environment ambient air, and (2) hand-held personnel leak locators. There should be at least one continuous detector for every chlorination station to prevent hazardous situations for both personnel and the surrounding population. Furthermore, these leak monitors are necessary to meet OSHA requirements for maximum contamination levels of chlorine (1 ppm) in the working area

The second category of detectors are for searching or checking for leaks in the fabricated components of the chlorine supply system which is under chlorine equilibrium vapor pressure

Since the continuous monitors are for area leaks, more than one detector per installation may be required For example, one each should be provided for tank car and/or storage tanks area, ton cylinder room, evaporator–chlorinator room, and at the discharge of chlorine vent lines Remote injector locations do not warrant a detector Most leak detectors are designed as single-point samplers, therefore multiple sampling point units should be used for detection at multiple sources Fig 9-32 illustrates the single-point system and Fig 9-33 shows the central system module capable of monitoring multiple sensors for a variety of sampling points

*Capital Controls.* The Advance Series 1030 detector uses a totally solid-state gas sensor [14] It consists of an electronic enclosure which contains the alarm and warning circuits and a remote sensor These two components are required for each area sampling point as shown in Fig. 9-32 The sensor is a solid-state voltammetric type based upon proprietary electrochemical gas-sensing electrodes Each sensor contains a sensing electrode and a reference electrode immersed in an electrolyte bound in an absorbant matrix No chemicals are required, thus eliminating any need for regular maintenance The Series 1030 is designed to permit a separation

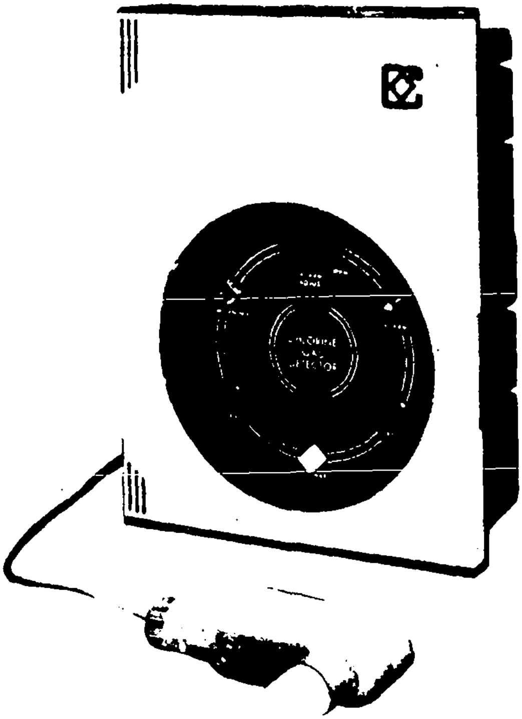

Fig. 9-32 Chlorine leak detector and sensor (courtesy Capital Controls Co )

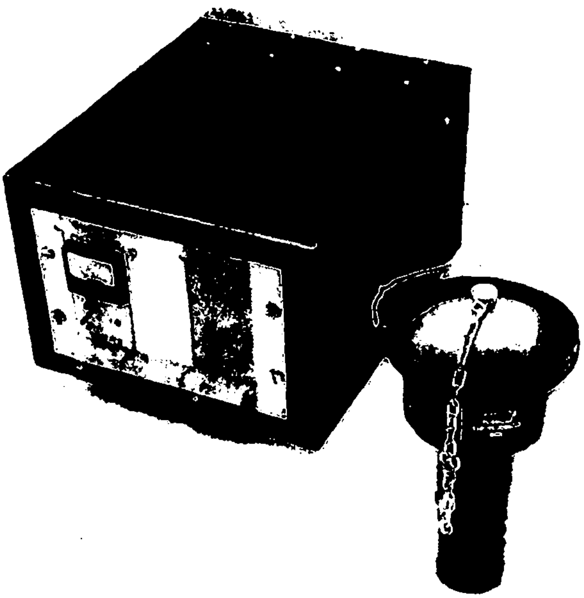

Fig. 9-33. Draeger Safety-Chloralarm (courtesy Draeger International and ICI, U.K.).

up to 3000 feet between the sensor and the electronics enclosure. The electronic circuitry is arranged to provide a dual monitoring system such that separate alarm and warning circuits provide redundant chlorine detection with backup alert in the event of either a slow accumulation of vapor or a major leak.

The Series 1030 meets the OSHA maximum concentration level of 1.0 ppm chlorine allowed in working environments. It is field adjustable in the alarm mode from 0 to 10 ppm of chlorine in the air sample. The instrument response time is 30 seconds. It is responsive to chlorine concentrations less than 1 ppm. The detection of chlorine gas is accomplished by a voltage applied across the two electrodes embedded in the sensor cell. The voltage level is selected for the gas of interest. When chlorine is present an electric current flows between the electrodes. This event actuates the warning and/or alarm circuits. The sensor recovery time after chlorine exposure is 5 minutes.

*Draeger Safety Chloralarm.* This detector system was designed by ICI, the major producer of chlorine in the United Kingdom. The licensee in the USA is Draeger Safety, a division of National Draeger Inc.[15] The Chloralarm detector was designed specifically for multiple sample source detection. Fig. 9-33 illustrates a single source system with one sensor. Large systems are housed in a free standing cabinet with a viewing panel behind a lockable front door. Eight, sixteen, or twenty-four channel systems are available with a built-in power unit.

The Chloralarm is a typical amperometric wet chemistry system used primarily for large chlorination process industries and other large consumers. The remote cable-connected sensors can be located almost any distance from the central control module. Two platinum electrodes are immersed in an electrolyte containing a small concentration of calcium bromide. When the air sample contains chlorine an electric current flows through the cell. This current triggers the alarm system. The response time is about 30 seconds. The sensor is designed to be installed outdoors in adverse weather conditions which also serves to protect it from mechanical damage. The large electrolyte reservoir eliminates the need for frequent replenishment. Under normal industrial conditions the sensor should operate without attention, for at least one year.

The Chloralarm has a unique built-in system check. Each module is provided with a switch whereby the entire function of that module and its associate sensor may be checked without having to visit the remote sensor and without having to expose the sensor to chlorine gas. Operation of the system check switch disconnects the 600 mV supply and provides a 2 V pulse to the remote sensor. This pulse electrolyzes the bromide solution in the electrolyte, which releases bromine at the electrodes. The system responds as if it were receiving an equivalent amount of chlorine. If the Chloralarm indicates an alarm condition it demonstrates that the sensor, sensor cable, cell electronics, and alarm system are all in working order.

The control module contains a meter scaled 0–5, 0–10, 0–25, and 0–50 ppm together with potentiometers for setting two alarm levels (per sensor) plus toggle switches for displaying the alarm levels.

*Enterra.** This company markets a line of toxic gas sensors.** The chlorine gas detector is their Chlor-Guard Model No. 5152.[16] It incorporates a gas diffusion sensor which does not require any maintenance. This sensor generates a current directly proportional to the concentration of chlorine. Response time is 90 percent in 15 seconds, and the sensor may be located 500 ft from the alarm module.

The alarm module contains alarm lights, horn, and alarm relays. When a low level of chlorine gas is sensed the yellow warning light will flash, and where a higher level of chlorine concentration is detected the red lamp will glow steadily. The concentrations of chlorine gas at which these alarms occur are adjustable on-site from 1 to 10 ppm.

The Enterra toxic gas sensors are classified as voltammetric, diffusion-limited electrochemical devices. Each sensor contains a noble metal sensing electrode and a reference electrode immersed in a supporting acidic electrolyte. A diffusion membrane isolates the sensing electrode from the ambient air. In operation a small voltage is applied across the two electrodes, the voltage level being a function of the gas of interest. When the sensor is exposed to chlorine in the ambient air,

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* Formerly Exidyne.

** See schematic Fig. [illegible] sulfur dioxide detector.

diffusion begins This allows the gas into the sensor through the diffusion membrane When the gas comes in contact with the polarized sensing electrode, an oxidation reaction occurs at the counter (reference) electrode This reaction generates a current in the system which is proportional to the concentration of chlorine gas at the diffusion membrane-sensor interface The electrode reactions for chlorine are:[17]

Sensing electrode

$$Cl_2 + 2e \rightarrow 2\,Cl \tag{9-2}$$

Counter electrode:

$$Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e \tag{9-3}$$

*Fischer and Porter* Their model series 17CA 1000 Chloralert is a low-concentration ambient-air chlorine detector[18] The detection level is fixed at 1 ppm chlorine by volume (3 mg/m$^3$) This instrument will sense and alarm at chlorine levels below the threshold of olfactory detection to conform to OSHA maximum tolerable limit

The Chloralert uses a glycerine-based electrolyte containing a small amount of potassium bromide. Dual platinum electrodes are partially immersed in the KBr* electrolyte A low voltage is applied across the electrodes which intensifies the electrochemical response.

An internal blower draws an air sample into the unit where it passes through a flow indicator to permit adjustment of the sampling rate. From the flowmeter the air sample flows to the electrode sensing cell where an electric current is generated by the presence of minute concentrations of chlorine. This current is sensed and monitored by a self contained electronic circuit and is used to trigger the alarm system The instrument response time is a matter of 2–3 seconds, and it desensitizes equally fast once the leak disappears.

Once the Chloralert is actuated, the circuitry is specifically designed to demand the alarm to be acknowledged with the spring-loaded reset switch. If the air sample still contains chlorine above the 1 ppm level, the alarm contacts will transfer to their normal (non-alarm) position while the reset switch is depressed and will immediately return to the alarm position when the reset switch is released. The test switch, when depressed together with the reset switch, substitutes a simulated sensing cell current, thus allowing a sample check to be made of the circuit performance

This instrument is designed for single sample point application and is limited to 25 feet from the source of air sampling. The sensing cell is designed for electrolyte replacement once per year

*Wallace and Tiernan.* The Wallace and Tiernan Series 50-125 Chlorine Detector consists of a dual electrode sensor and an electronic package which controls and

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* When chlorine comes in contact with this electrolyte $Br_2$ is released by the oxidation action of chlorine The free bromine triggers the alarm circuit

monitors the sensor.[19] The sensor unit is provided with a 5-liter electrolyte reservoir. This administers a drip rate flow of electrolyte which wets the surface of the dual electrodes. The reservoir has enough capacity for about 3 months continuous operation. The electrolyte contains a small amount of potassium iodide (KI) in solution with glycerine and distilled water. A 0.4 voltage is applied across the dual platinum electrodes. This sharpens the sensitivity and reduces the electrode response time, which is a matter of 2–3 seconds. This detector is available in three sensitivities: 0.5, 1.0, and 3.0 ppm chlorine in air.

When the concentration of chlorine in the air sample reaches or exceeds the detection level, the red alarm light will remain on until the chlorine concentration recedes below the detector sensitivity. When the alarm condition has been eliminated, the sensor should be cleaned and wetted with electrolyte again by using the wash bottle supplied with the unit. This speeds up the return of the detector to normal (non-alarm) operating condition. The detector circuitry can be tested by actuating the "PRESS TO TEST" button on the front panel. The red alarm light should go on. The sensor electrodes must be coated with the electrolyte-otherwise the detector will not alarm for chlorine. Therefore the drip rate of the electrolyte must be checked by the operator on a frequent basis. The drip rate will vary with temperature and barometric pressure changes. The electrolyte in the supply reservoir is protected from ambient air contamination by an activated carbon filter. Whenever the detector is exposed to a high concentration of chlorine, the filter should be replaced.

This detector is designed for single-source air sampling. It is equipped with a built-in motor driven fan which draws the air sample into the sensor cell. The air sample source should be limited to 25 ft from the detector location and not lower than 4 ft from the sensor elevation.

*Leak Locators.* American Gas and Chemical Co., Northvale, NJ markets two products that assist the operator in locating chlorine, ammonia or sulfur dioxide leaks. These products are identified by number for each specific gas.

For chlorine, CDP-100 is a chlorine-sensitive spray which reacts chemically with minute chlorine leaks causing a visible color change from white to yellow at the point of leak. It is easily removed with a damp cloth.

For personnel protection and leak searching there is a rechargeable, hand-held detector model CGT-701. This instrument can locate chlorine leaks as low as 1 ppm. It uses a solid-state sensor which requires no maintenance and cannot be poisoned.

**Expansion Tanks.** These tanks are mandatory for liquid chlorine supply systems. These chambers are necessary when there is danger of liquid chlorine becoming trapped in a length of pipe. If this situation is followed by a significant ambient temperature rise then hydrostatic pressure will develop. This may be sufficient to rupture the pipe because the coefficient of expansion of steel is much less than that of liquid chlorine The recommended type of expansion tank with rupture disc and chlorine pressure switch as recommended by the Chlorine Institute is illustrated in Fig. 9-12. The frangible disc ruptures at pressures between 300 and 400 psi, thereby allowing the liquid trapped in the system to enter the expansion tank. This immediately produces some vapor pressure in the expansion tank, which actuates the pressure switch and sounds the alarm. Spring loaded relief valves discharging to the atmosphere should never be used on liquid chlorine lines. The chance of such a valve reseating properly is remote. Therefore, the discharge of any and all such valves should be to an absorption system.*

## FLOW OF CHLORINE IN PIPES UNDER PRESSURE

The fluid mechanics of liquid and gaseous chlorine are entirely different, and so they will be discussed separately.

**Liquid Chlorine.** The flow of liquid chlorine is restricted to the piping between the supply containers and the evaporators. This flow of liquid will not be similar to that of other liquids. For this reason, the friction loss of flowing liquid chlorine cannot be accurately predicted, as has been confirmed by field tests with rates of liquid chlorine flow up to 18,000 lb/day in approximately 1000 ft equivalent length of 1" Sch. 80 pipe.[20] This is due to the phenomenon of the liquid chlorine "flashing" to vapor whenever there is a sudden change of the flow rate in the system. Most chemical processes function at some fairly precise optimum capacity, but a chlorinator facility is designed to have a wide range of flow capability—at least twenty to one.

Therefore, when there is a sudden change in the flow rate, the liquid in the evaporators suddenly vaporizes rapidly, causing an abrupt pressure drop in the system, due to the change in demand. The vaporization process will extend back into the pipeline leading from the storage containers and create pockets of gas impeding the flow of the liquid. This vapor flashing occurs first at points of highest friction loss, such as entrance and exits of valves and fittings.

Finally, after the vaporization becomes stabilized in the evaporators, the pressure will rise in the evaporators, causing the flashing to cease in the pipeline. Then the system performs normally until there is another abrupt change in the liquid chlorine flow rate. The longer the pipeline, the longer the system takes to stabilize In a 500 ft line, the pressure will begin to restore itself in about five to ten minutes, depending on the rate of flow change, and will take two or more hours for complete restoration of pressure. This phenomenon is also related to temperature. If the chlorine pressure in the storage tank is at 80 psig, then the vapor temperature would be only 68°F. A long liquid line on a warm day or one exposed to the sun might be considerably warmer than 68°F, which would tend to warm the chlorine above its vapor pressure and to cause flashing in the line. The line would,

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* Exception: See "Evaporater Relief System" p. 637

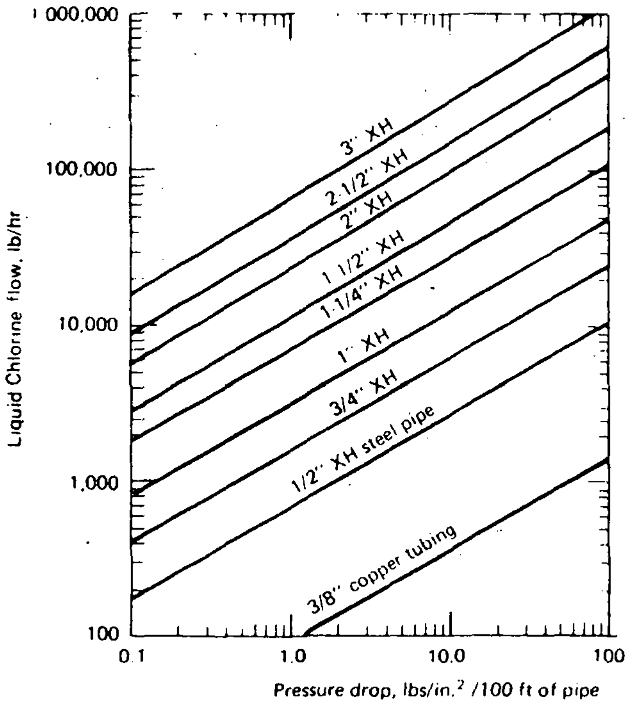

Fig. 9-34. Friction loss in liquid chlorine piping. (Clean new pipe; vaporization in the pipes will cause much higher drops.) (courtesy Hooker Chemical Co.)

however, be cooled by the flow of liquid chlorine, and the flashing would cease when sufficiently cooled below the vapor pressure. Therefore, depending upon the ambient temperature, the pressure in the chlorine containers, and the rate of change of liquid flow in the system, many combinations of pressure fluctuations will be noted. Sudden pressure drops of 10 to 15 psi in a 1" line 500 to 1000 ft long, with a maximum flow of 24,000 lb/day would not be unusual. Flows of 24,000 lb/day and less are considered "low" by chlorine manufacturers. This is only 1000 lb/hr, compared with the excess flow rate valve restricting withdrawal rates from tank cars at 7000 lb/hr.

Fig. 9-34 shows the estimated pressure drop in various size pipes carrying liquid chlorine. On the basis of sudden changes in flow under various kinds of climatic conditions and container pressures, it is recommended that the pipe size be limited to a maximum pressure drop of 0.25 psi per 100 ft for lines 500 ft and longer and of 0.5 psi per 100 ft for shorter lines. Thus, the following size lines should be limited to the capacities shown in Fig. 9-34:

| | *Maximum Liquid Cl₂ Flow lb/Day* | |
|---|---|---|
| | *Length of Line* | |
| *Line Size* | *Less than 500 ft* | *500–1500 ft* |
| ¾" | 24,000 | 17,000 |
| 1" | 48,000 | 33,600 |
| 1¼ | 100,000 | 72,000 |
| 1½" | 168,000 | 115,000 |

Actually, ¾" pipe should not be used for lines longer than about 100 ft. Furthermore, most manufacturers have standardized on 1" inlets and outlets for the various chlorine piping accessories. While the flows shown in Fig. 9-34 may seem enormous for such small lines, it should be noted that the velocity of liquid chlorine in a 1" pipe at 48,000 lb/day is only slightly more than 1 ft/sec.

*Example:*

$$V \text{ ft/sec} = \frac{Q \text{ cu ft/sec}}{A \text{ sq ft}} \tag{9-4}$$

The inside diameter of a 1" Sch. 80 pipe is 0.957"

$$A \text{ sq ft} = \left(\frac{0.957}{12}\right)^2 \frac{\pi}{4} = 0.00499 \text{ sq ft}$$

$Q$ 48,000 lb chlorine per day, so

$$\frac{48{,}000}{1440 \text{ min} \times 60 \text{ sec}} = 0.5556 \text{ lb/sec}$$

Liquid chlorine at 68°F weighs 87.8 lb/cu ft; so

$$Q = \frac{0.5556}{87.8} = 0.00632 \text{ cu ft/sec}$$

Therefore

$$V \quad \frac{0.00632}{0.00499} = 1.27 \text{ ft/sec}$$

Therefore the figures given in Fig. 9-34 are conservative for liquid chlorine pipe systems. The designer is cautioned to be meticulous about arriving at the proper equivalent length of pipe, accounting for elbows, sudden enlargements, ammonia unions, tees for pressure gages, switches, and line valves Most of these values are given in the Appendix to the present book

The flashing phenomenon of liquid chlorine is one reason the flow cannot be properly measured. The usual differential pressure method for measuring the flow of liquids, including the variable area meters (rotameters) cannot be properly calibrated since the basic principle of their operation depends on a pressure drop which initiates the flashing phenomenon. At this point, there are both gas and liquid, with entirely different flow characteristics, passing through the measuring device simultaneously Under proper conditions, a rotameter will give at best a rough approximation The conductivity factor of liquid chlorine is so low that magnetic meters cannot be used either.

**Gaseous Chlorine.** Since the flow of chlorine gas follows the laws of fluid dynamics, the friction loss in such a system can be predicted with reasonable accuracy.

In pipelines carrying gas, the designer should have two special concerns: the piping system from the evaporators to the chlorinators, and the line carrying the gas from the chlorinator to the injector under a vacuum. When remote injectors are used, this calculation of line size is critical because the head loss tolerance is low—1½ to 2" Hg vacuum. The chlorinator is relying on the injector for its operating energy, so that little should be wasted in friction loss. However, on the pressure side between the evaporators and chlorinator, a 10 psi pressure drop can be tolerated. A critical situation develops when the velocity of the gas under pressure is so great that it undergoes sufficient cooling to cause condensate or ice formation on the outside of the pipe.* Therefore if the velocity is kept below 35 to 40 ft/sec, this phenomenon will probably not occur and the pressure drop will be easily tolerable.

Most manufacturers arrange for one evaporator to serve each chlorinator independently. The openings out of the evaporator are 1"; the chlorine filters and regulating valves are also made for 1" pipe. Therefore the pipe size for any 8000 lb/day chlorinator and evaporator should always be 1" Let us investigate the velocity and possible head losses that will occur at maximum output of the chlorinator.

Gas leaving the evaporator will be at approximately 100°F. Let us assume a gage pressure of 85 psi, indicating that the gas has a certain amount of superheat, which is normal for a properly operating evaporator.

The density ($\rho$) of the gas = 127 lb/100 cu ft (See Fig. 1, Appendix)

$$Q = 8000 \text{ lb/day} = 0.0926 \text{ lb/sec}$$

Converting to cu ft/sec

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* As the gas cools it becomes denser and the friction loss increases

$$\frac{0.0926 \text{ lb/sec}}{1.27 \text{ lb/cu ft}} = 0.0729 \text{ cu ft/sec}$$

Now

$$V = \frac{Q}{A}, \qquad A \text{ for a 1'' Sch. 80 pipe} = 0.00499 \text{ sq ft}$$

so

$$V = \frac{0.0729 \text{ ft}^3\text{/sec}}{0.00499 \text{ ft}^2} = 14.6 \text{ ft/sec}$$

This tolerable velocity exists between the evaporator and the external chlorine pressure-reducing and shut-off valve. (See Fig. 9-35.) Downstream of the CPRV,

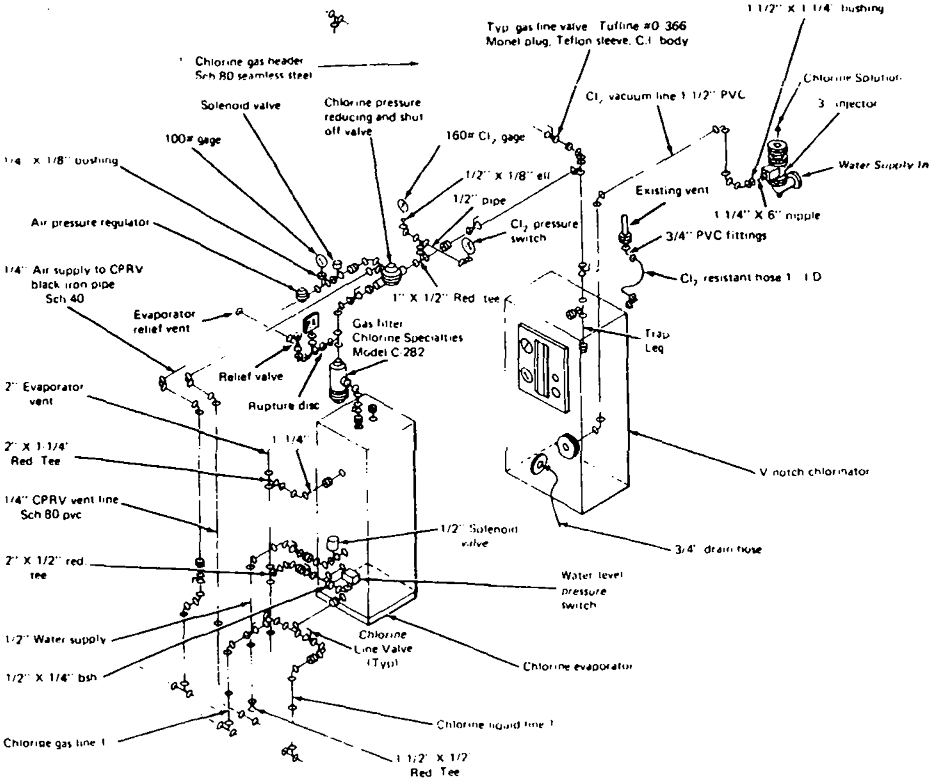


Fig. 9-35. Piping schematic evaporator, filter, CPRV, and chlorinator Chlorine gas and liquid line fittings are 2000 lb forged steel. All unions on chlorine gas and liquid piping are ammonia type with lead gasket.

conditions change abruptly. Usually the CPRV is adjusted to give a downstream pressure of 40 to 60 psi. Let us now see what the velocity is at the reduced pressure of 40 psi. The temperature of the gas will drop about 25°F owing to this pressure reduction, so that the density of the chlorine gas will be $\rho = 0.7$ lbs/cu ft. Therefore

$$Q = 8000 \text{ lb/day} = 0.0926 \text{ lb/sec} = \frac{0.0926}{0.7} = 0.1325 \text{ ft}^3\text{/sec}$$

and

$$V = \frac{0.1325}{0.00499} = 26.51 \text{ ft/sec}$$

As the velocity increases, the pressure drop due to friction losses increases exponentially. This further reduction in pressure reduces the density of the gas, thereby initiating further increase in the velocity, which further compounds the friction loss problem. The above velocity, 26.5 ft/sec, will not cause excessive friction losses in a conventional layout, but does approach the upper limit of maximum allowable velocity.

The rule of thumb for designing chlorine gas supply systems is to limit the velocity at maximum flow to 50 ft/sec and preferably not more than 35 ft/sec.

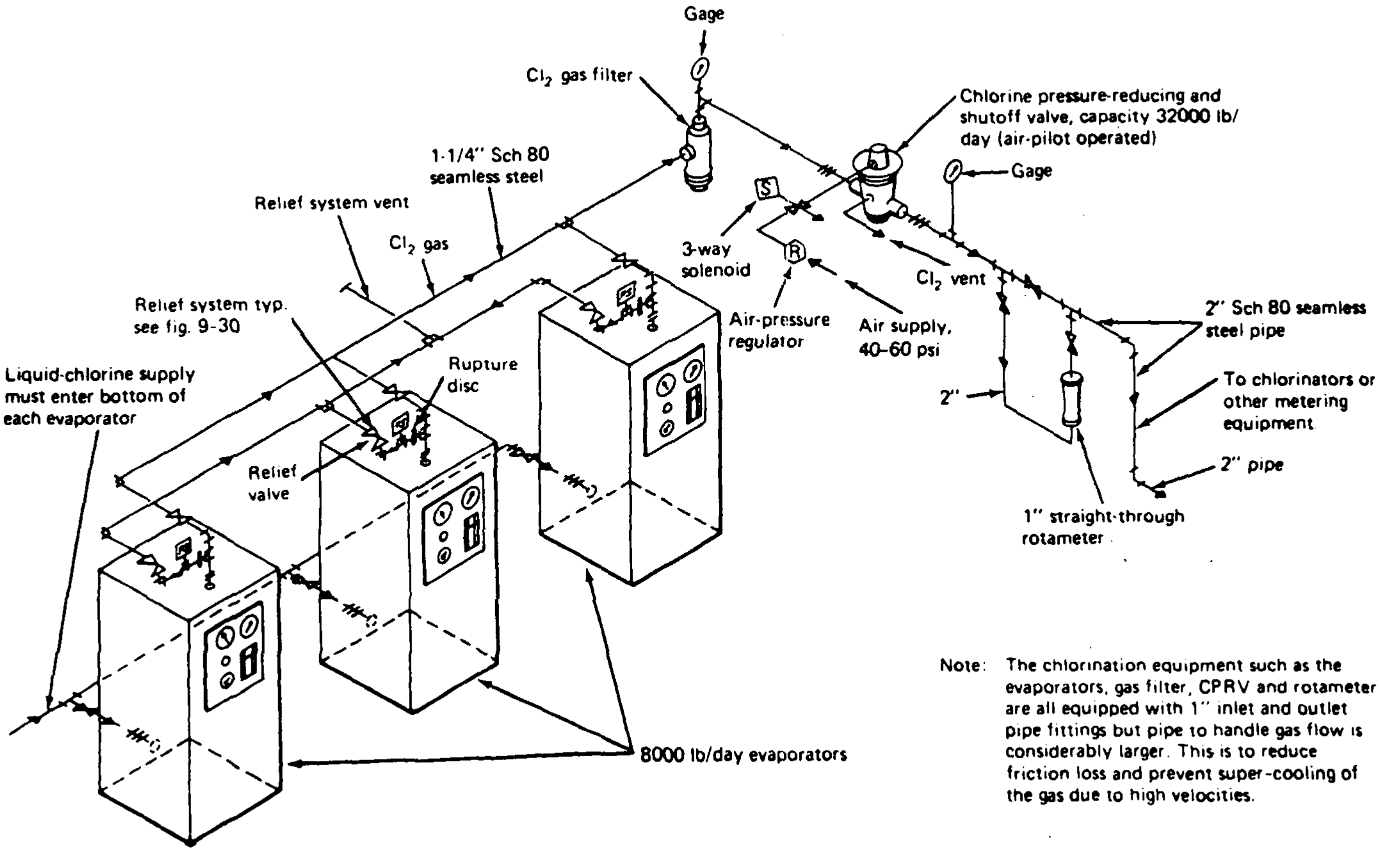
Whenever evaporators are manifolded together, the designer must provide piping large enough to stay below this velocity limit. In these instances the rotameter and chlorine pressure-reducing valve will have 1" pipe size connections, as will the chlorinator, but the piping required may have to be 2".

As an example, consider the case of manifolding three evaporators, capacity 8000 lb/day, discharging to a common header through a CPRV, thence through a transmitting rotameter, for recording and totaling the chlorine flow, and thence to each of three chlorinators, as illustrated in Fig. 9-36. Note that the CPRV has a 1" inlet and outlet, but has a nominal capacity of 32,000 lb/day. Similarly, a 1" straight-through metal tube rotameter can easily handle 24,000 lb/day of chlorine. It is permissible to allow the high velocity of chlorine gas through these two devices, but the rest of the piping must be at least 1½".

The gas will cool from the inlet temperature at the CPRV from 90 to 100°F down to an average of about 65 to 70°F between the CPRV and the chlorinator. The CPRV will be adjusted to give a downstream pressure of approximately 35 psi at 24,000 lb/day flow. This gives a chlorine gas density of approximately 0.65 lb/cu ft.

Using 1½" pipe, we get

$$Q = 24{,}000 \text{ lb/day} = 0.2778 \text{ lb/sec} = \frac{0.2778}{0.65} = 0.4265 \text{ ft}^3\text{/sec}$$



Note: The chlorination equipment such as the evaporators, gas filter, CPRV and rotameter are all equipped with 1" inlet and outlet pipe fittings but pipe to handle gas flow is considerably larger. This is to reduce friction loss and prevent super-cooling of the gas due to high velocities.

Fig. 9-36. Manifold chlorine evaporators. The chlorination equipment, such as the evaporators, gas filter, CPRV, and rotameter, is all equipped with 1-in. inlet and outlet pipe fittings, but pipe to handle gas flow is considerably larger. This is to reduce friction loss and prevent super-cooling of the gas owing to high velocities.

and

$$V=\frac{0.4265}{0.01225}=34.82 \text{ ft/sec}$$

This is close to the upper limit of velocity, which starts a vicious cycle: as the velocity increases, the gas becomes cooler; as the gas cools, it becomes denser, thus increasing the friction loss. As the friction loss increases, it becomes more and more difficult to regulate the density through the rotameter in order to maintain its calibration.

The equivalent length of pipe between the CPRV and chlorinator may be as high as 60 ft, even though the two units are no more than 10 to 15 ft in pipe length apart, depending upon the number and kinds of fittings in the piping layout.

Another method of analysis is to use Reynolds number ($N_r$), a dimensionless quantity that relates velocity, viscosity, and size of pipe. It can be expressed in the following ways:[21]

$$N_r=\frac{pVD}{u'}=\frac{6.32\ W}{ud} \tag{9-5}$$

where

$V$ = velocity, ft/hr
$D$ = diameter, ft
$W$ = mass flow, lb/hr
$d$ = diameter, in
$p$ = density, lb/cu ft
$u$ = viscosity, cp
$u'$ = viscosity, lb/hr-ft
$u' = 2.42u$

Taking the case of 24,000 lb/day flow in a 1" pipe, Reynolds number is calculated as follows:

$$N_r=\frac{6.32\times 1000}{0.0127\times 0.957}$$

The temperature of the gas at this velocity in a 1" pipe will drop to about 40°F; hence $u = 0.0127$ cp and therefore

$$N_r=654{,}600$$

Not let us make the same calculation for the case where the maximum recommended allowable velocity in 1" pipe is two evaporators manifolded together = 16,000 lb/day flow. therefore

$$N_r = \frac{6.32 \times 666.7}{0.0129 \times 0.957}$$

The temperature of the gas at this velocity in a 1" pipe will be about 50°F; hence $u = 0.0129$ cp, and therefore

$$N_r = 364,175$$

Now for the 24,000 lb flow in a 1½" pipe which shows a velocity under the 50 ft/sec maximum limit, Reynolds number will be

$$N_r = \frac{6.32 \times 1000}{0.0131 \times 1.500} = 321,630$$

The temperature of the gas at this velocity is estimated to be approximately 60°F.

*It would appear that the size of the pipe must be such that the Reynolds number is kept below 365,000 for any piping system between the CPRV and the chlorinator.*

## CHLORINATORS

### Historical Background (See Also Chapter 6):

*Direct Gas Feed.* The first gas chlorinators developed circa 1906–10 were of the direct gas feed type. No matter how ingenious or competent the design, these chlorinators suffered disastrously from flooding by water at the point of application. This occurred in spite of a negative head at the point of application. Maintenance due to corrosion was excessive to say the least.

*The Suck-Back Phenomenon.* This occurrence is related to the affinity chlorine has for water. If the chlorine feed is shut off or if the feed rate is low enough (<0.25 lb/day), chlorine gas in the feed line adjacent to the diffuser will gradually be absorbed by the water. If this condition persists a vacuum begins to build up in the feed line, which will eventually pull the water from the point of application all the way back to the chlorine cylinder—in spite of the vapor pressure in the cylinder! This is the suck-back phenomenon that plagued all direct-feed chlorinators until special corrosion-resistant back-pressure valves were designed to prevent this occurrence.

*The Bell-Jar Era* In an all-out effort to solve the two major problems of chlorine gas metering, the suck-back phenomenon and impurities in the gas, C. F. Wallace developed the vacuum solution-feed bell-jar line of chlorinators. This line of chlorinators enjoyed great success from circa 1922 to about 1960. Fig. 6-2 (Ch. 6) illustrates a flow-paced automatic unit—maximum capacity 500 lb/day. The operation of the chlorine pressure reducing valve was visible inside the bell jar. The vacuum created by the injector was transmitted to the bell jar, where chlorine impurities present were spewed into the glass jar and could be easily retrieved for analysis. The evidence provided by operators of these chlorinators resulted in the production of a special "clean" grade of chlorine for water supplies, wastewater, and cooling waters. The suck-back phenomenon was resolved by the incorporation of the vacuum relief system which automatically allowed air to enter the chlorinator, thereby breaking any vacuum that might result from suck-back. All solution-feed chlorinators today have vacuum relief systems. The two salient points that were responsible for the success of bell-jar chlorinators were: (1) they were made entirely of corrosion-resistant materials, and (2) the opration was completely visible. Their major disadvantage was feed-rate capacity limitation. For feed rates in excess of 500 lb/day the design became complicated, which resulted in excessive production cost.

## Development of the Spring-Loaded Diaphragm Concept:

*General Discussion.* The famous bell-jar line of chlorinators pioneered by Wallace and Tiernan was replaced virtually overnight by the introduction of PVC injection molding. Once again the original spring diaphragm concept was revived and its success was made possible by the research into plastics and corrosion-resistant diaphragms, particularly by DuPont. The very first series of chlorinators marketed by Wallace and Tiernan were based upon the spring-loaded diaphragm principle (ca 1913). Owing to severe corrosion problems this concept was dropped as soon as the visible vacuum models by C. F. Wallace were introduced (ca 1920). When PVC injection molding and teflon diaphragms became available the chlorinator design approach reverted to the original spring-loaded diaphragm principle, utilizing the technology of the newly arrived plastics industry (ca 1955).

This design concept, pioneered by Fischer and Porter, was a much needed stimulus for the chlorinator industry. This was a small specialty manufacturing industry at that time, but once the ingredient of quality competition was introduced the results for the consumer were dramatic. To counter the impact of the Fischer and Porter "all plastic" line, Wallace and Tiernan introduced their line of "plastic" chlorinators but with a revolutionary idea of chlorine feed-rate control. Wallace and Tiernan introduced the V-notch orifice concept, which they had been keeping under wraps for at least 10 years. This concept of chlorine metering control proved to be unique. From this point forward Wallace and Tiernan developed unbelievably accurate and flexible control systems. Their success spurred their competitors to greater achievements, some of which are described below.

*Theory of Operation.* These chlorinators consisted of the following components:

1. Inlet chlorine pressure-reducing valve
2. Indicating meter (rotameter)
3. Chlorine metering orifice
4. Manual feed rate adjuster
5. Vacuum differential-regulating valve
6. Pressure-vacuum relief valve
7. Injector

Figure 9-37 is a flow diagram of a Wallace and Tiernan V-800 chlorinator illustrating a "pressure" type system as opposed to the remote vacuum arrangement. The chlorine gas enters the system through the pressure-vacuum regulating valve at which point the inlet chlorine pressure from the supply system is reduced to some constant level of negative (vacuum) pressure (the level of vacuum varies with each manufacturer). The gas then passes through the metering orifice (V-notch) to the differential vacuum regulator and then to the injector vacuum line.

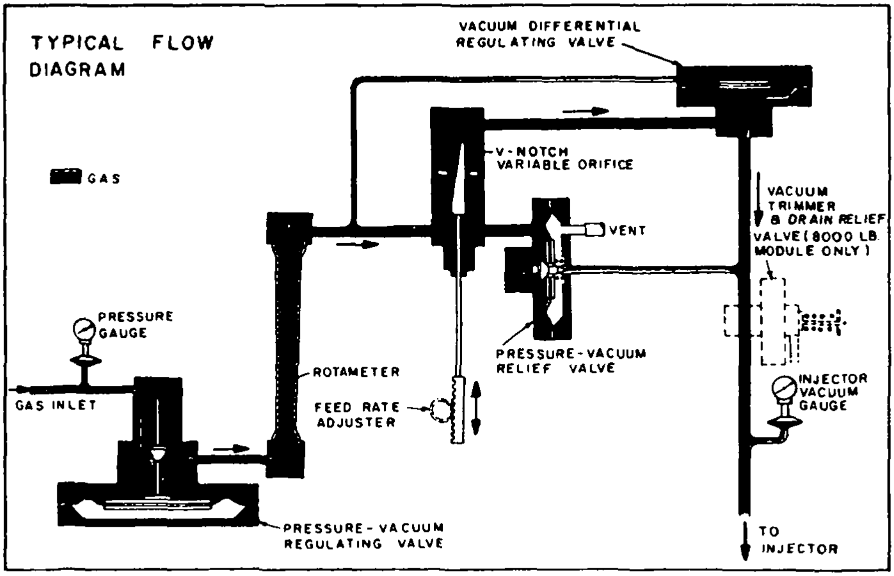


Fig. 9-37 Flow diagram V-800 series vacuum solution feed chlorinator (courtesy Wallace and Tiernan Div Pennwalt Corp.).

The chlorine flow through the V-notch orifice is based upon the classic flow formula $Q = AV$ where $A$ is the area of the orifice opening (position of V-notch orifice positioner) and $V$ is the velocity of the gas through the orifice. This gas velocity is best expressed in terms of the differential pressure across the orifice to produce a given velocity. This is equal to $C\sqrt{2gh}$, where $h$ equals the differential vacuum across the differential vacuum regulator and $C$ is the velocity coefficient of the V-notch orifice. The pressure–vacuum regulating valve illustrated in Fig. 9-37 is designed to maintain a constant pressure (usually a slight vacuum) upstream from the metering orifice and control device. The vacuum differential regulating valve is designed to maintain a constant pressure drop ($h$) across the metering orifice (V-notch orifice).

*Sonic Flow Concept.* The most recent development in chlorinator design which affects accuracy and control modes is the concept of sonic flow. Previously described concepts assumed that the gas flow through the metering orifice (feed-rate valve) was a function of the differential pressure across that valve ($h$). This is true for a wide range of differential pressures; however, if the velocity through the valve is increased to the speed of sound in the gas flow at that point, a different set of conditions is encountered. Once the sonic velocity is reached, the flow through the valve is no longer a function of the pressure drop ($h$) across the valve. Under these conditions, gas flow is directly proportional to the area of opening in the control valve and is entirely independent of the downstream pressure, which is a function of the injector vacuum. Therefore, when sonic flow conditions are attained, the differential vacuum regulator is no longer a necessary component of chlorinator design. Fig. 9-38 illustrates a typical sonic flow design by Capital Controls. Sonic

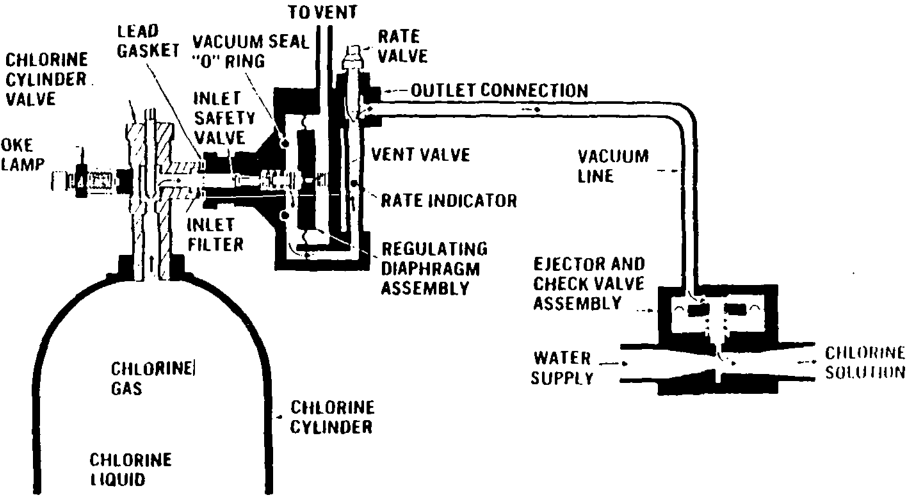


Fig. 9-38 Flow diagram sonic flow type chlorinator (courtesy Capital Controls Co.).

flow chlorinators are limited to 2000 lb/day capacity owing to the additional energy required by the injector systems to achieve sonic velocities across the chlorine feed-rate valve.

*Remote Vacuum* This is a concept whereby the chlorine supply system operates under a vacuum from the cylinder to the inlet of the injector. Originally the advantage of this arrangement was to increase the margin of safety in the handling of chlorine. However, this is a minor benefit, because analysis of chlorine emission accidents indicates that the supply piping is rarely a factor in these occurrences. The major benefit is the use of the remote vacuum concept for automatic cylinder switchover. Remote vacuum systems are available up to 8000 lb/day as shown in Fig. 9-39.[22] This is of doubtful value because the system is applicable only with the vapor phase. An 8000 lb/day chlorinator requires an evaporator, therefore the vapor under pressure travels only a short distance where space is at a premium for mounting the vacuum regulating valve and pressure-check, and pressure relief

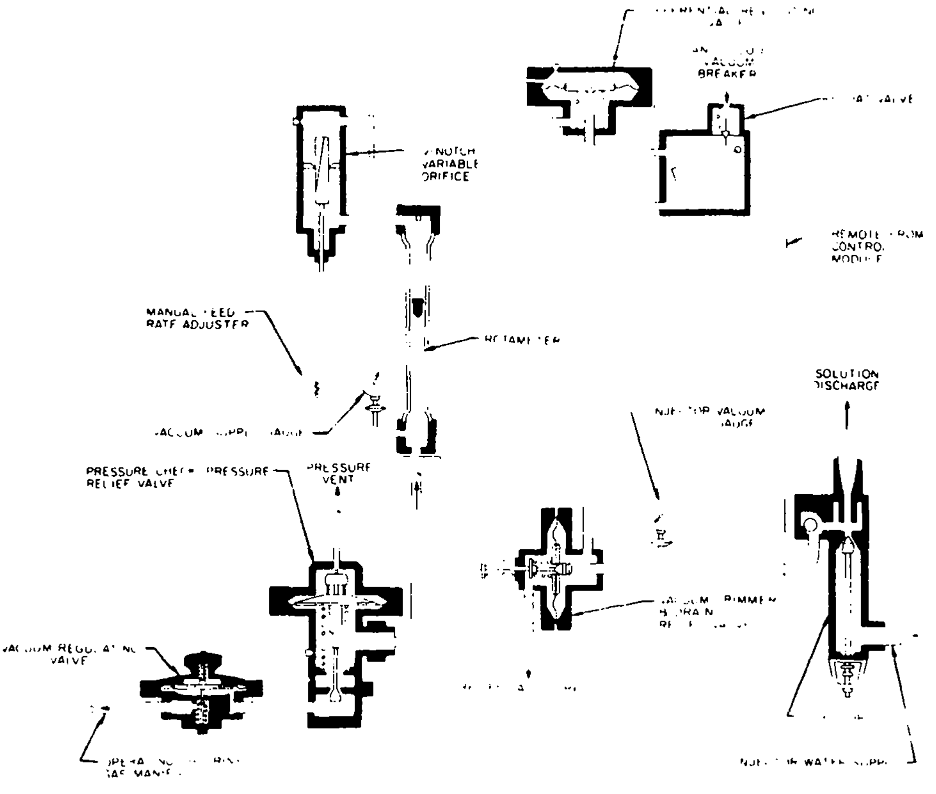


Fig. 9-39 Flow diagram remote vacuum system for 8000 lb/day chlorinator (courtesy Wallace and Tiernan Div. Pennwalt Corp.)

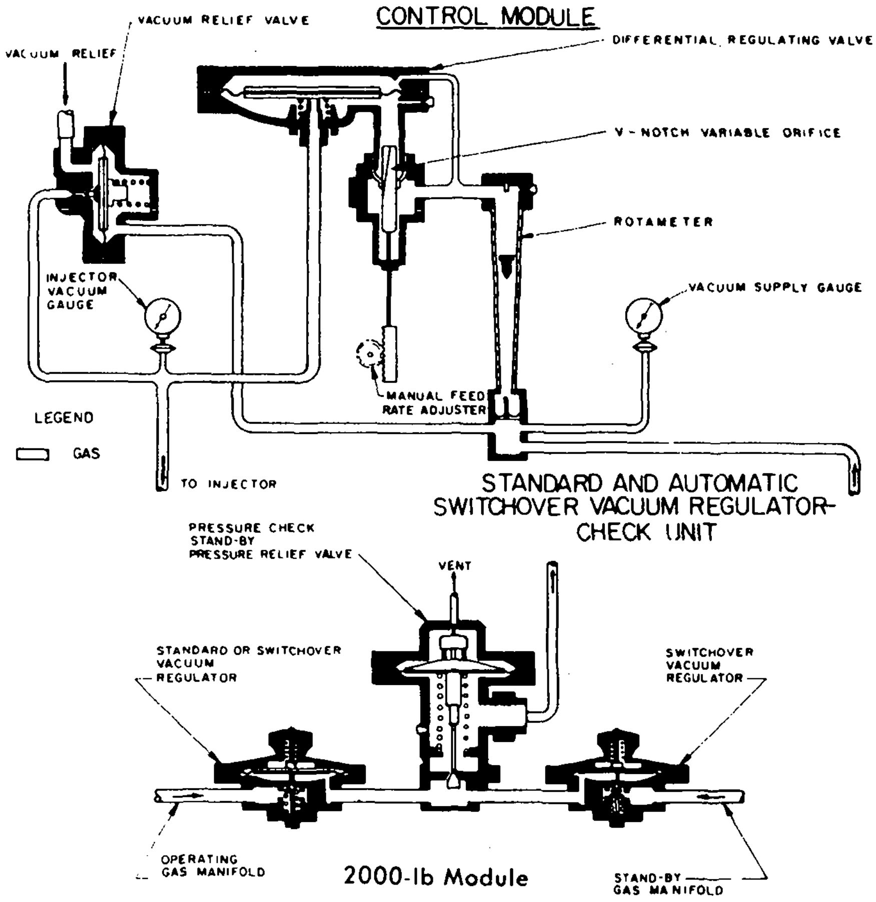


Fig. 9-40. Flow diagram of combination remote vacuum and automatic switchover system; 2000 lb/day chlorinator (courtesy Wallace and Tiernan Div. Pennwalt Corp.)

valve Therefore when liquid is used instead of vapor the chlorinator should be arranged as shown in Figs. 9-11 and 9-37 with the pressure–vacuum regulating valve located within the chlorinator cabinet.* The 8000 lb/day unit (Wallace and Tiernan) utilizes a combination vacuum-trimmer and drain-relief valve in combination with an anti-flood vacuum breaker instead of a conventional vacuum relief valve. The 500 lb and 2000 lb Wallace and Tiernan chlorinators use a conventional vacuum relief valve with the remote vacuum arrangement as shown in Fig. 9-40.[22]

It should be noted that although remote vacuum capability is available up to 8000 lb/day, automatic switchover by the remote vacuum principle is limited to 2000 lb/day capacity *Pressure sensing for automatic switchover is available for any capacity*

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* This arrangement is currently available only on special order

## Control Strategies:*

*General Discussion.* All chlorinators are arranged for basic manual control. This control is accomplished by opening and closing a valve characterized for a nominal range of 10:1 Most manufacturers provide rotameters calibrated over a 20:1 range. Chlorinator models are usually separated into capacity categories of 100, 500, 2000, and 8000 lb/day Some manufacturers stretch the capacity of the 8000 lb/day size to 10,000 lb/day, depending upon certain site conditions.

For each of the models described above there is a variety of metering tubes and other internal accessories available to cover the entire capacity range of each category For example, for a 2000 lb chlorinator, the available rotameter tube sizes are: 50, 75, 100, 150, 250, 500, 1000, 1500, and 2000 lb/day.

*Flow Pacing.* This is accomplished by the use of an analog signal transmitted from the process flow meter to the motor drive on the shaft that positions the chlorine metering orifice. This valve is designed and characterized so that the flow of chlorine varies *directly* as the process flow changes. Therefore the signal transmitted by the process flow meter must be linear with process flow. This signal can be either electric (4–20 MA) or pneumatic (3–15 psi). In the Wallace and Tiernan chlorinators the chlorine orifice valve is commonly referred to as the V-notch plug. The Fischer and Porter valve is known as the Chloromatic valve. Depending upon local conditions an optional item for flow paced control is the use of a ratio relay This is desirable when the primary meter is oversized for future conditions.

> EXAMPLE. A treatment plant is designed for 50 mgd in the year 2000. Current peak daily demand is only 20 mgd. Install a ratio relay with a range of 0.4–4.0 in order to get the full range of the chlorinator.

When considering flow pacing by itself there is tradeoff between range and accuracy A chlorine dosage that is flow paced only will only be as accurate as the transmitted flow signal The accuracy of this signal depends upon the primary metering element. Designers should specify the accuracy they want over a specified range, i.e., 3:1, 5:1, 10:1 Many makers of primary elements are reluctant to claim ±2 percent accuracy over a range that exceeds 4:1. This is a crucial factor in precise chlorine dosage control It is discussed in further detail below.

*Direct Residual Control.* For new systems where retrofitting is not a problem, this method has considerable appeal. The key elements that make up a successful operating system are (1) selection of proper injector water pump, (2) careful design of chlorine diffuser and residual sample tap, and (3) a short loop time.

The appropriate way to describe the direct residual control concept is by an example A 48 inch pipe carries an average daily flow of 12 mgd and summer peaks of 24 mgd Low flow during the early morning hours is 2 mgd. This represents

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* See Appendix for control function definitions

a 12:1 flow range and a velocity range of 0.31–2.96 ft/sec The first step is the diffuser design to provide proper initial mixing at the point of chlorine injection. Assume chlorine dosage will be a maximum of 2.5 mg/l This amounts to 500 lb/day at 24 mgd flow This is the upper limit for a fixed-throat injector, so choose a 2 inch adjustable throat injector capable of passing at least 70 gpm. This is for mixing reasons, as will be shown. Use an across-the-pipe diffuser as shown in Fig. 9-40a with two cluster jets of three holes each pointing upstream. Using the Egan concept of upstream jet energy for mixing, design chlorine diffuser perforations for 25 ft/sec velocity This requires six ½" holes at 12 gpm per hole for a total amount of injector water of 72 gpm. This diffuser will develop a head loss of 11.75 ft

The next step is to calculate the $G$ factor

$$G = \sqrt{\frac{550 \times P}{\mu V}} \tag{9-6}$$

$$P = \frac{Qh}{3960} = \frac{72 \times 11.75}{3960} = 0.21 \tag{9-7}$$

In order to calculate $G$ the volume of the initial mixing area affected by the energy of the jet will have to be decided. Experience in wastewater chlorination indicates that mixing will occur in 2–3 seconds. The longer the time selected for mixing, the lower the $G$ value will be. Assume 3 sec at average flow, 12 mgd, where $V = 1.48$ ft/sec. This means the mixing volume is 55.77 ft³.

$$G = \sqrt{\frac{550 \times 0.21}{2.35 \times 10^{-5} \times 55.77}} = 296.86$$

The next step is to calculate $G$ for the dissipation in energy caused by the counterflow—this is called the Egan effect. Referring to Fig. 9-40a it is assumed that the obstruction of the 3-inch diffuser with the two cluster jets and the impinging effect of the cluster jets will dissipate some of the energy in the 12 mgd counterflow. The diffuser restriction increases the velocity of the mainstream from 1.48 ft/sec to 1.65 ft/sec and $V^2/2g = 0.04$ ft. Assume a head loss of 0.04 ft in the mainstream at this point.

$$P = \frac{8343 \text{ gpm} \times 8.34 \times 0.04}{60 \times 550} = 0.08 \text{ hp}$$

and

$$G = \sqrt{\frac{550 \times 0.08}{2.35 \times 10^{-5} \times 55.77}} = 183.23$$

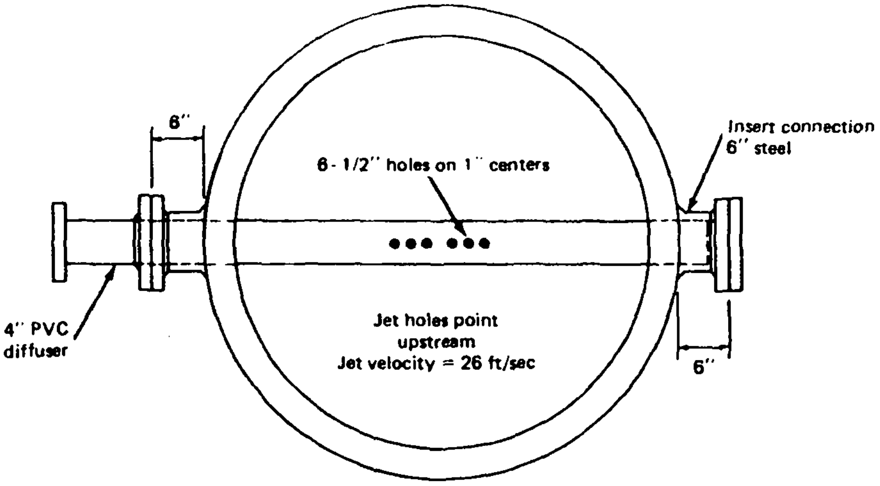


Fig. 9-40a. Egan type cluster-jet counterflow diffuser

Therefore it is reasonable to believe that the total energy dissipated can be translated into a $G$ factor equal to the jets 297 plus the counterflow 183 for a total $G = 480$. This amount of turbulence is sufficient for adequate mixing.

*Sampling Tap.* The downstream sampling tap which is also the injector pump suction should be a duplicate of the chlorine diffusers with the holes pointing upstream, except that the number of holes must be increased to reduce head loss to one ft. This arrangement will insure that the sample received by the analyzer will be consistently homogeneous. Moreover, using the injector pump in this fashion will tend to short-circuit the main line flow in such a way as to prevent abnormally low velocities during low flow periods. See Fig. 9-41

*Loop Time.* Estimating the loop time (system response) is the next step. Referring to Fig. 9-41, the loop-time circuit is defined as *A-B-C-D-E*. The travel time through all of these segments will be constant by design except from *A-B* and *C-D*. These segments of the loop will vary with the velocity of chlorine in the vacuum line and of water in the 48 inch pipe from low flow to peak flow conditions.

From Fig. 9-41 use the following distances:

$A\text{-}B = 300$ ft
$B\text{-}C = 30$ ft
$C\text{-}D = 10$ diam. $= 40$ ft
$D\text{-}D_1 = 10$ ft
$D_1\text{-}E = 15$ ft

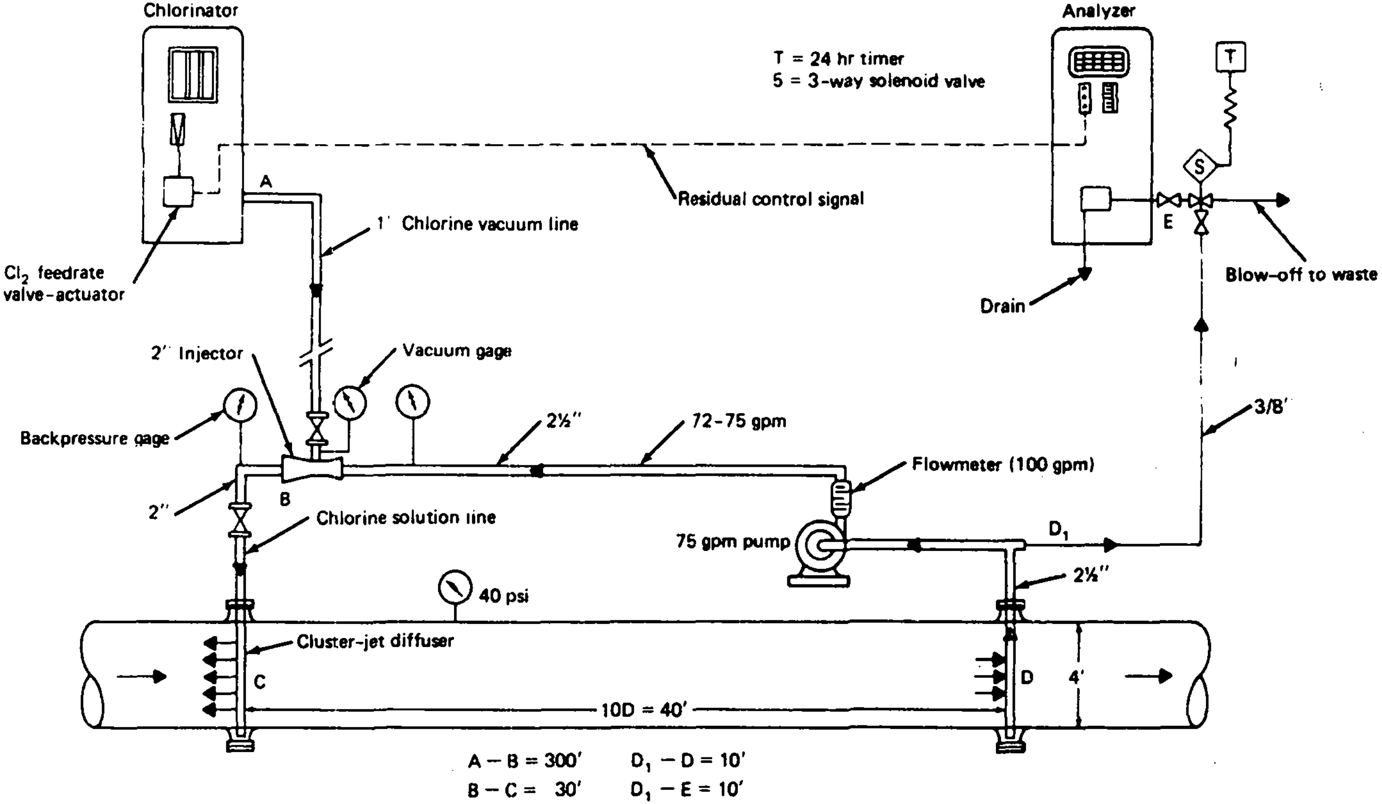


Fig. 9-41. Direct residual control system using injector water pump to provide analyzer sample which minimizes control loop dead time.

Injector pump flow by pump selection and control valve will be 72–75 gpm. Sample flow to the analyzer pump suction will be 1 gpm and pressure in 48 inch pipe is estimated at 40 psi

The next step is to calculate the flow in each of the segments:

1 *A-B*, chlorine gas flow at 500 lb/day max Try a 1 inch PVC vacuum line:

$$Q = 500 \text{ lb/day} = 0.0115 \text{ lb/sec}$$

Density of $Cl_2$ gas at injector vacuum of 20 in Hg = 0.06 lb/ft³

$$Q = \frac{0.0115}{0.06} = 0.1917 \text{ cfs}$$

and

$$V = \frac{0.1917}{0.005} = 38.34 \text{ ft/sec}$$

Now calculate for friction loss to see if 1 inch pipe is large enough:

$$P = \frac{11.89 \times L \times f \times (W)^2}{10^9 \times P \times d^5} \tag{9-8}$$

where

$L$ = equiv length of vacuum line, ft
$f$ Darcy's friction factor
$p$ = density of chlorine gas, lb/ft³
$d$ diameter of pipe, inches

The next step is to find the friction factor $f$ by calculating the Reynolds Number:

$$N_R \quad \frac{6.32 \times W}{u \times d \times 24}$$

where

$u$ viscosity of chlorine gas = 0.0133.

$$N_R \quad \frac{6.32 \times 500}{0.0133 \times 0.957 \times 24} = 10345$$

From Fig 8 (Appendix) the friction factor $f$ = 0.07 Therefore

$$P = \frac{11.89 \times 300 \times 0.07 \times (500)^2}{10^9 \times 0.06 \times (0.957)^5}$$

$$= 1.3 \text{ in Hg}$$

so 1″ line is big enough. Therefore at 500 lb/day the gas velocity will be about 38 ft/sec and at low flow, 40 lb/day, the vacuum will be higher and the gas less dense.

$$Q = 40 \text{ lb/day} = 0.00046 \text{ lb/sec}$$

$$Q = \frac{0.00046}{p} = \frac{0.00046 \text{ lb/sec}}{0.03 \text{ lb/ft}^3} = 0.01543 \text{ cfs}$$

so

$$V = \frac{0.01543}{0.005} = 3.06 \text{ ft/sec}$$

Therefore the travel time for the chlorine in the vacuum line will vary from 100 sec at 40 lb/day rate to 8 sec at 500 lb/day. However, the response time following a dosage change occurs at a rate of 50 percent change in the first 25 percent of the time required to achieve the total dosage change of, say, 100 sec at 40 lb/day chlorine feed rate. For example, if the controller called for a 5 lb/day rate change at the 40 lb/day feed rate, the response time in the vacuum line to change the feed rate to 42.5 lb/day would be about 25 percent of 100 sec or 25 sec. This demonstrates the necessity to keep the chlorinator module as close to the injector as possible. *It also demonstrates that remote vacuum and automatic switchover systems should be designed so that the vacuum line between the chlorine supply system and the chlorinator be kept to a minimum,* i.e., not more than ± 15 ft.

2. *B-C.* This is the chlorine solution line and diffuser segment. The injector should be as close as physically possible to the diffuser inlet. Assume a distance of 10 ft. At 72–75 gpm the velocity in a 2 inch pipe will be about 8 ft/sec and will cause a head loss of about 1.5 ft. The response time for this segment will be negligible—about 1 sec.

3. *C-D.* This is the 40 ft length of 48 inch pipe between the chlorine diffuser and the pump suction which is also the sampling tap. At peak flow rate (24 mgd) $V = 2.96$ ft/sec and travel time to sample tap = 14 sec. at low flow (2 mgd) $V = 0.25$ ft/sec, so travel time will be 160 sec to the sample tap.

4. $D$-$D_1$. This is the segment where the sample is carried in the pump suction which is a 3 inch pipe. Assume this is 10 ft. At 75 gpm, $V = 3.4$ ft/sec, so travel time is a constant 3 sec.

5. $D_1$-$E$. This segment is the sample line to the analyzer from the injector

pump suction. The flow requirement to the analyzer is only 1 gpm maximum. Therefore use a ⅜ in. PVC pipe (brass or copper not allowed). The velocity in this pipe will be 1.67 ft./sec at 1.0 gpm. Assume this pipe is 10 ft long. Travel time will be a constant 6 sec.

Table 9-7 summarizes the response time elements. This represents a 9:1 change in response rate for a 12:1 flow treatment range. It is obvious that a great improvement can be made if the chlorinator could be moved to shorten the vacuum line to a reasonable distance of 10–20 ft. However, this wide range of response can be handled by a proper control system. It is recommended, however, that the upper limit of response time for low flow conditions should never exceed 5 min.

Table 9-7 Loop Time

| | *Loop Segment* | *Low Flow (2 mgd), seconds* | *Peak Flow (24 mgd), seconds* |
|---|---|---|---|
| *A-B* | $Cl_2$ vacuum Line | 100 | 8 |
| B-C | $Cl_2$ solution Line | 1 | 1 |
| *C-D* | 48 in. pipeline | 160 | 14 |
| *D-D₁* | Sample line, pump suction | 3 | 3 |
| *D₁-E* | Sample line to analyzer | 6 | 6 |
| Total loop time | | 270 | 32* |

* Response time for the sample within the analyzer is about 15–20 seconds

An embellishment would be to use an alternative sample point for flows less than 5 mg/day, located 20 ft downstream from the diffuser. This is usually unsatisfactory because the sample tends to be stratified with various levels of chlorine residual. Moreover, since this is an exercise in direct residual control the above concept requires a flow meter to switch the valves on the two pump suction points.

The control system shown in Fig. 9-41 requires the electric valve operator for the chlorinator feed rate to be able to change the feed rate from zero to maximum in at least 15 seconds. The analyzer is required to have a 4–20 mA transmitter which will provide a linear signal from zero to full scale residual over a specified range of 0–1, 2, 5, 10, or 20 mg/l chlorine residual. This signal is transmitted to an adjustable residual set point controller with proportional, integral (reset), and derivative control functions. This controller drives the chlorine feed-rate valve. Potable water chlorination systems have been known to operate well on a 0.1 mg/l dead band where the residual span is 0–2 mg/l. One wastewater plant has operated successfully with a dead band of 0.2 mg/l where the residual span is 0–5 mg/l.[23]

A most important requirement in the operation of continuous residual analyzers is the necessity to purge the sample line at frequent intervals in order to scour away the biological slimes that are prone to build up in the sample lines. Referring to Fig. 9-41 there is shown a sample blow-off line controlled by a timer. The purging cycle should be once every 24 hours for 2–3 min. The orifice on the downstream side of the ⅜ inch solenoid valve should be a ⅜ × ¼ reducer ending in about 6 inches of ¼ inch pipe.

The injector water pump for the system shown will be required to have a TDH of approximately 60 psi to provide 100 psi inlet pressure to the injector.

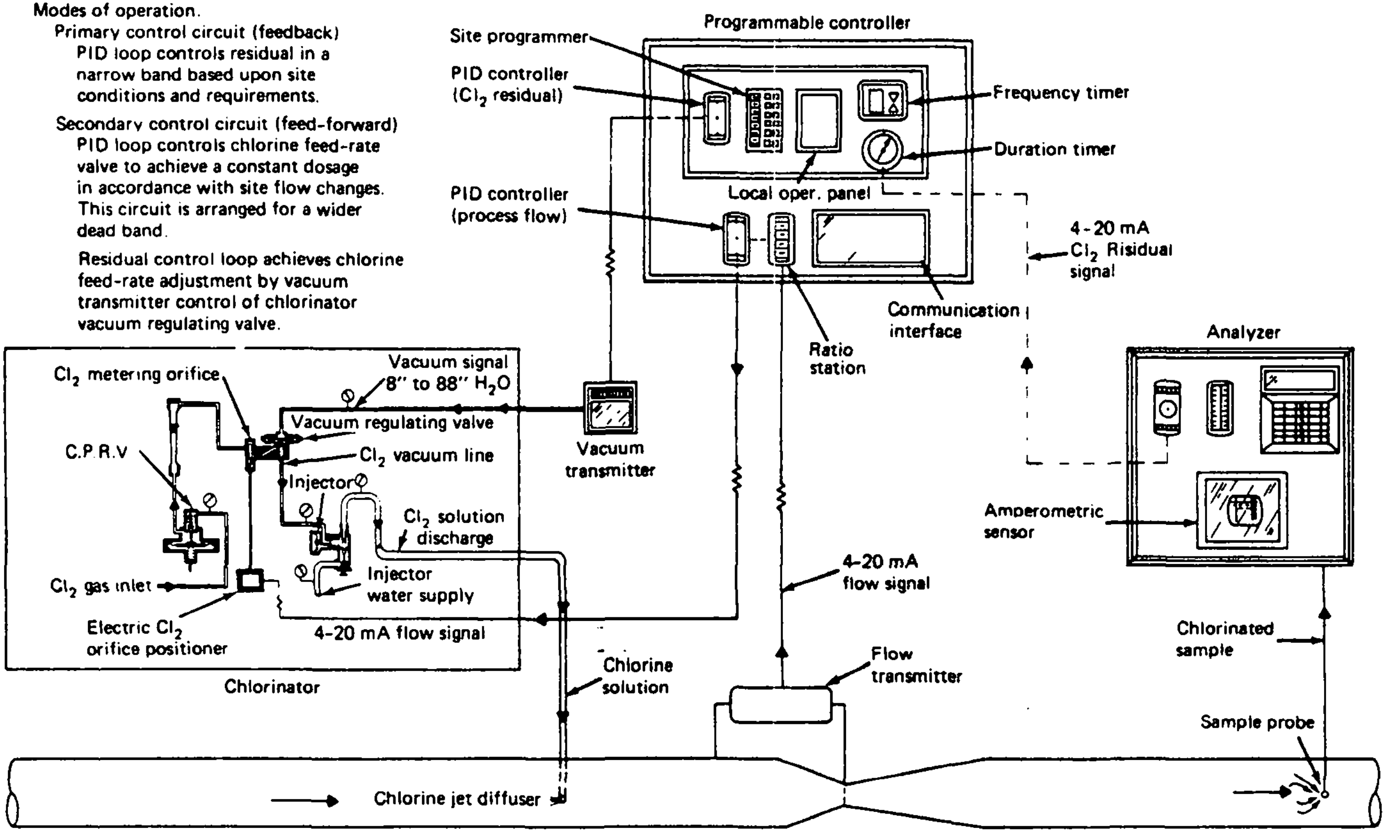
*Compound Loop Control.* This control strategy was first introduced in 1960 by Wallace and Tiernan Inc. (U.S. Patent No. 2,929,393). The control scheme is based upon two separate but independent signals, so that each can change the chlorine feed rate separately. One signal represents process flow changes and the other registers chlorine residual changes. The first chlorine residual control for a wastewater plant utilized this system.[79] The installation was at the Napa Sanitary District treatment plant, Napa, CA in 1961. Since that time there have been several hundred such installations. However, in 1984 Wallace and Tiernan elected to drop this system in favor of the remote vacuum method. Since the compound loop system is being used extensively and since it can be made available on special order the following discussion is deemed worthwhile.

The difference between this method and other systems using two signals is as follows: each signal controls a different component within the chlorinator, and each performs an independent chlorine feed-rate change by a different function of gas flow mechanics. Other systems using dual signals integrate the two signals by external instrumentation which transmits a single multiplied signal to the chlorine feed-rate valve. (Exception: the Fischer and Porter Chloromatic feed-rate valve contains built-in multiplier instrumentation.)

As illustrated by Fig. 9-42 the process flow signal is transmitted to the motor-operated chlorine feed-rate valve and the chlorine residual signal goes to the vacuum differential regulating valve. This concept is based upon the fundamental law of fluid mechanics: $Q = AV$, where $Q$ = chlorine flow, $A$ = area of the chlorine orifice opening, and $V$ = velocity through the orifice. The velocity through the orifice follows the following law of fluid mechanics: $V = \sqrt{2gh}$, where $h$ is the head loss required to initiate a gas flow change. In this method $h$ is the vacuum differential across the chlorine orifice which is controlled by the vacuum differential regulating valve.

*Chlorine Feed-Rate Valve.* This component is described by Wallace and Tiernan as the V-notch orifice positioner. The motor drive is capable of changing the feed rate from zero to maximum in 15 seconds. There is an internal feedback loop which controls and verifies valve travel for any signal from 4 to 20 mA. This valve is controlled by the signal from the primary flow meter.

*Vacuum Differential Regulating Valve.* This valve changes the chlorine feed rate by changing the vacuum differential across the chlorine rate valve orifice. On Wallace and Tiernan equipment the vacuum range is from 8 to 88 in. $H_2O$, zero to maximum feed rate. This vacuum level can be controlled by a vacuum



Modes of operation.

Primary control circuit (feedback)
PID loop controls residual in a narrow band based upon site conditions and requirements.

Secondary control circuit (feed-forward)
PID loop controls chlorine feed-rate valve to achieve a constant dosage in accordance with site flow changes. This circuit is arranged for a wider dead band.

Residual control loop achieves chlorine feed-rate adjustment by vacuum transmitter control of chlorinator vacuum regulating valve.

Fig. 9-42. Compound-loop residual control system using a programmable controller.

transmitter capable of changing the vacuum over the complete range in about five seconds. This vacuum level can also be controlled by a motorized vacuum valve which has a much slower vacuum rate change, approximately 15 minutes from 8 to 88 in. $H_2O$. This provides floating control by a cycle and duration timer.

Table 9-8 illustrates the mathematics of variable vacuum control as a function of chlorine feed rate. This is informative because it is recommended procedure to adjust the vacuum level of the vacuum regulator in the mid-range or 50 percent of valve travel. This is shown as 28 inches $H_2O$ vacuum.

*Theory of Operation.* Fig. 9-42 illustrates a potable water chlorination system which was retrofitted from flow pacing control to compound loop control using a programmable controller to perform the intelligence functions. The programmable controller for each chlorinator installation requires the control strategy to be designed for specific field conditions. This particular system described by Fig. 9-42 had the following characteristics:

1. The chlorinator was located at the outlet of a reservoir where reverse flow occurred on a daily basis.
2. Water flow meter in a 60 inch concrete pipe had a range far exceeding any practical use, 0–200 cfs. The actual flow range in the high demand season was from 10 to 120 cfs—a 12:1 range.
3. The piping configuration was such that upstream supplies entering this pipeline occasionally contributed some measurable chlorine residual.

## Table 9.8 Arithmetic of Variable Vacuum Control Wallace and Tiernan Equipment

| | | | | *Vacuum Signal to Chlorinator, in. $H_2O$ (Variable Vacuum + Fixed Vacuum = Total)* | | |
|---|---|---|---|---|---|---|
| *Chlorine Feed Rate, %* | *Chlorine Flow as a Factor* | *Vacuum Differential = $Cl_2$ × Flow* | *Chlorine Flow as a Factor = $Cl_2$ Flow$^2$* | *Flow Factor × Range* | *Fixed Vacuum Zero Signal* | *Vacuum Gage in. $H_2O$* |
| 100 | 1.00 | 100 | 1.00 | 80 | 8 | 88 |
| 90 | 0.9 | 81 | 0.81 | 64.8 | 8 | 72.8 |
| 80 | 0.8 | 64 | 0.64 | 51.2 | 8 | 59.2 |
| 70 | 0.7 | 49 | 0.49 | 39.2 | 8 | 47.2 |
| 60 | 0.6 | 36 | 0.36 | 28.8 | 8 | 36.8 |
| 50 | 0.5 | 25 | 0.25 | 20.0 | 8 | 28.0 |
| 40 | 0.4 | 16 | 0.16 | 12.8 | 8 | 20.8 |
| 30 | 0.3 | 9 | 0.09 | 7.2 | 8 | 15.2 |
| 20 | 0.2 | 4 | 0.04 | 3.2 | 8 | 11.2 |
| 14.3 | 0.143 | 2 | 0.02 | 1.6 | 8 | 9.6 |
| * | | | | | | |
| 10 | 0.1 | 1 | 0.01 | 0.8 | 8 | 8.8 |
| 0 | 0 | 0 | 0 | 0.0 | 8 | 8.0 |

* Practical limit of usable range = 7:1

Owing to the above characteristics it was decided to use the PC in the following manner:

1 Primary control was a PID feedback loop between the chlorine residual analyzer and the vacuum transmitter This loop controlled the chlorine flow through the vacuum differential regulator This control loop was designed with a narrow dead band.

2 Secondary control was achieved by a second feed forward PID loop which controlled the chlorine feed-rate valve to provide a constant dosage (lb Cl/cfs) all in accordance with water flow information from the flow meter This loop was designed to operate on a wider dead-band. This loop was only for abrupt flow change corrections. If an alarm condition occurred for *X* seconds or minutes the feed-rate valve motor would open or close for *N* seconds.

3. If the chlorine residual level entered the PID alarm zones for *X* seconds the mathematical constant that converts the water flow rate to chlorine dosage (lb Cl/cfs) units is changed causing a greater or lesser dosage when the feedforward loop operates. This dosage computation change protects the system from wide variations of chlorine demand due in part to chlorine residuals in the system upstream from the chlorine diffuser

4. The reverse flow sensor system shuts down the chlorinator for a specific length of time to allow for flow oscillation to cease. The chlorinator is restarted when steady outflow occurs. Reverse flow detection can be performed by the use of an auxiliary analyzer or a thermal probe sensing system. See "Reservoir Outlets" in this chapter.

5. The loop time for the chlorination system was determined in the field. It was 2 min 25 sec at 47 cfs. Deducting the travel time from *C* to *D* at 47 cfs the loop time constant calculated to 1.62 min. From this loop time characteristic the correction cycle frequency exhibited a variation from 2.0 min at 120 cfs to 5.5 min at 10 cfs and up to 11 min at flow reversal conditions.

6. The next step was to determine the required length of correction duration for an arbitrary dead band setting of 0.25 mg/l on the residual control PID loop. Using a 1000 lb chlorine rotameter and allowing each correction to be one-half the dead band or 0.125 mg/l, the chlorine feed-rate change required for each correction from 5 to 120 cfs flow is shown in Table 9-9 Since the chlorine feed-rate valve response is a constant at about 50 lb/sec it was decided to use a wider dead band for flow pacing control so that at about 30–40 cfs flow the chlorine feed-rate adjustment would be taken over by the residual control loop, where the feed-rate change can be as low as 10 lb per correction. Table 9-9 itemizes the chlorine feed-rate change per correction based upon one-half the dead band change in dosage = 0 125 mg/l.

Using the loop time information developed on site, the PC can be programmed with mathematical constants so that the chlorine feed rate change will respond quickly and accurately to wide flow fluctuations and chlorine demand changes The use of dual PID loops provides greater flexibility over the wider range of

## Table 9-9 Chlorine Feed-Rate Change per Correction

| *Water Flow* | | | |
|---|---|---|---|
| *cfs* | *mgd* | *Cycle (min)* | *$Cl_2$ Flow Change, lb/day* |
| 120 | 77.5 | 2.0 | 80.60 |
| 110 | 71.1 | 2.0 | 73.94 |
| 100 | 64.6 | 2.0 | 67.18 |
| 90 | 58.2 | 2.5 | 60.53 |
| 80 | 51.7 | 2.5 | 53.77 |
| 70 | 45.2 | 2.5 | 47.01 |
| 60 | 38.8 | 2.5 | 40.35 |
| 50 | 32.3 | 2.5 | 33.54 |
| 40 | 25.8 | 3.0 | 26.83 |
| 30 | 19.4 | 3.0 | 20.18 |
| 20 | 12.9 | 3.5 | 13.42 |
| 10 | 6.5 | 5.5 | 6.76 |
| 5 | 3.2 | 9.5 | 3.33 |

conditions. Assuming that the PID flow pacing loop has a ±3 percent accuracy over a 4:1 flow range and the residual control loop has at least a 7:1 range, a worst case situation is provided with at least a 28:1 range—far in excess of normal necessity. Other features of this type of dual signal control include the ability to isolate and operate manually each of loops either locally or remotely in case of analyzer failure.

The most important feature is the automatic takeover by the residual control loop when the process flow drops below the accurate range of the flow meter. More than 20 years of operating experience has demonstrated that this method of dual signal feedback control is a favorite with operating personnel because it is easy to adjust, calibrate, maintain, and understand.

When restarting the system or when recalibrating, the operator manually positions the vacuum valve to read 28 in. $H_2O$ vacuum. This is followed by adjusting the chlorine feed-rate valve to give the appropriate chlorine dosage. The PC allows site-specific corrections and adjustments to account for loop time and historical flow patterns. Dual adjustable dead bands provide more flexibility and greater reliability of the control system.

### Dual Signal Control Systems:

*Introduction.* This type of control strategy employs the use of two separate signals multiplied together to produce a single output which controls the chlorine feed-rate valve within the chlorinator. This is the method used by the three most active chlorinator manufacturers. This strategy is described in various ways, including compound loop control. It is not, however, the same as the compound loop control system described above

In order to compare the systems offered by the different manufacturers *a common chlorination problem in potable water treatment was presented to them.* The strategies described for each manufacturer were based upon the following field conditions:

A 60 inch reinforced concrete pipe, served by a balancing reservoir, has an existing chlorine diffuser and a residual sample tap already in place. A venturi meter with a dp transmitter which generates a 4–20 mA output signal is located nearby. The flowmeter range is 0–200 cfs; however, historical records show that maximum flow has never exceeded 120 cfs. Low flows are on the order of 5 cfs due to almost flow reversal conditions.

The loop time at 47 cfs has been established as 2 min 25 sec. The distance from the chlorine diffuser to the residual sample point is 116 ft. Chlorine dosage is approximately 0.75 mg/l. The flow signal is not considered reliable under 50 cfs. Assuming one correction per loop time, frequency of correction will vary from 2 min up to 7 min.

*Capital Controls Co.* This firm announced a new, scientifically advanced chlorinator control system in 1984.[24] Fig. 9-43 shows a simplified schematic of this system. It is described by the manufacturer as a compound-loop control system, but it should not be confused with the Wallace and Tiernan compound loop system described above. It is a dual signal system which controls only one component in the chlorinator—the feed-rate valve.

*Controller.* The entire control system is shown in Fig. 9-44. It is packaged in a cabinet so that the operator can perform all the one-time adjustments, system calibration and residual set point adjustments from one convenient location.

The process water flow signal is modified by a dosage control adjustment (ratio station). It is a one-time set based upon flowmeter range and chlorine feed-rate valve sizing. The second signal, the residual signal, is compared to the set point. If the residual is at the set point no corrective action occurs. When corrective action is required an error signal is transmitted to the deviation gain. The deviation gain is a site-specific field adjustment (one-time set) which reflects the characteristics of the system. The deviation gain provides a wide choice of speed response to the amount of the error signal. For example, it permits a 10 percent difference of signal from set point to be altered from one percent of valve travel to 100 percent of valve travel.

The valve correction signal is transmitted simultaneously to the proportional multiplier circuit and the integral/timing circuit. These two circuits provide independent functions. The proportional circuit permits a rapid valve response while the integral circuit provides slow fine-tuning.

The proportional multiplication function is the same as proportional band. It is field adjustable, site specific, one-time set to fit local requirements. The integral/timing circuit sets an internal time delay (lag) in sampling the residual error signal. The adjustment is set on site and must have a time period equal to or greater than the loop time. (For a description of loop time, see Fig. 9-41.)

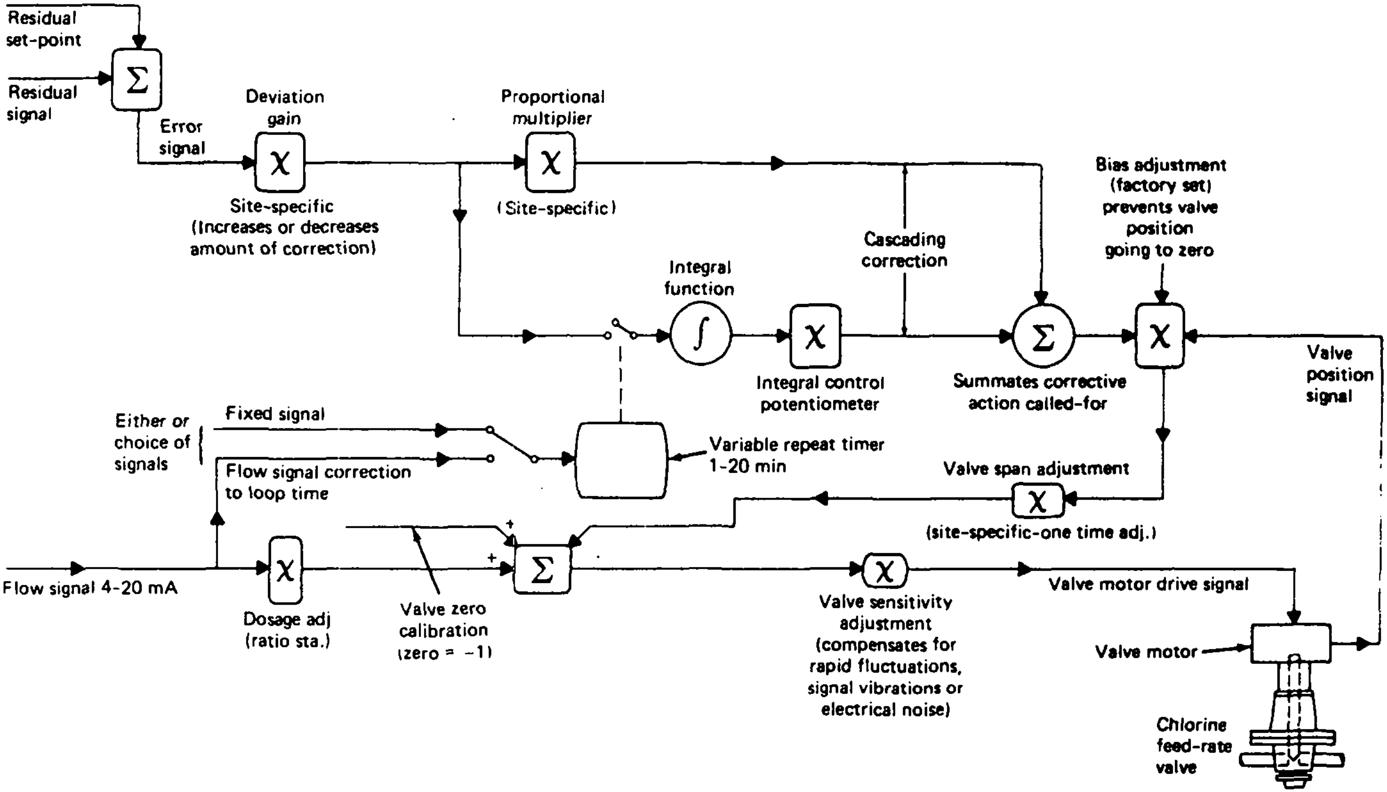


Fig. 9-43 Dual-signal residual control system (courtesy Capital Controls Co.).

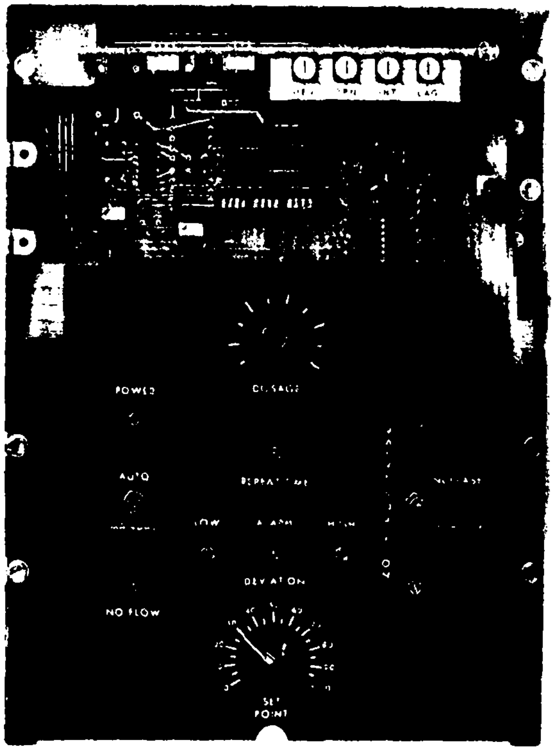


Fig. 9-44 Dual-signal control system electronic controller package (courtesy Capital Controls Co.)

The integral/timing circuit allows the valve to remain relatively dormant until the chlorine residual analyzer has time to measure a true sample. The lag adjustment varies frequency of correction. The length of correction is dependent upon the time taken by the rate valve to move to a new position. There is no change in output until a new correction signal is received after the lag-time cycle repeats. The lag time cycle frequency is arranged to be proportional to flow or set at a predetermined fixed value.

The integration circuit is the same as reset. It integrates or sums the error signal for a two second period after the lag-time cycle ends. The signal is held until the next lag-time cycle occurs and then recorrects itself. The integral function is the reset adjustment. It is field set for fine tuning at the time of startup.

At this point in the circuitry the signals from the proportional and integral loops are summed and the result is sent to a multiplier. This multiplier also receives a signal from the chlorine feed-rate valve feedback potentiometer.

A factory offset (bias) is added to permit the residual control function to override the flow proportioning function. This provides added protection and greater system reliability, particularly during low water flows or when the water flowmeter signal is erratic or unreliable.

The offset principle is described in the following mathematical model:

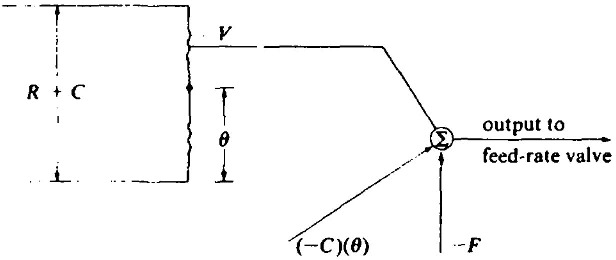
$$(R + C)\left(\frac{V}{100} + \theta\right) + (-F) + (-C) \times (\theta) = 0 \qquad 9\text{–}9)$$

$$V = \left[\frac{F - (R)(\theta)}{R + C}\right] 100 \qquad (9\text{–}10)$$

where

$R$ = residual control signal voltage
$C$ = factory set constant voltage (bias)
$\theta$ = constant ratio
$F$ = flow signal voltage
$V$ = valve position (percent)

Schematic of Mathematical Model



Equation (9–9) represents the summation of the input signals from chlorine residual, process flow, and the offset (bias)—which prevents the feed-rate valve from complete closure. (Chlorinators cannot be designed for zero flow conditions, except by interrupting the injector operation.) Eq. (9–10) represents the feed-rate valve position as percent open. This equation also shows how the residual control system can operate alone as a controller by modifying the bias signal to the chlorine feed-rate valve. The circuitry also allows the flowmeter control to act without residual control.

The multiplied signal has a valve span adjustment which is site-specific and usually a one-time set. This adjustment serves as a ratio station to trim a grossly over or undersized valve. The valve span is field adjustable.

Switches in the controller allow the operator to select any of these operating modes: manual, flow paced, flow paced-residual, residual alone, and dechlorination.

*Chlorine Feed-Rate Valve.* This is a constant-speed-motor driven linearized valve which requires approximately 70 seconds to travel from zero to 100 percent feed-rate position in 12½ revolutions. The valve can move physically through 16 turns. The valve also drives a ten-revolution geared feedback potentiometer. This allows fine positional resolution. One contact drives the motor upscale and another drives it downscale. The system operation is as follows: the controller sends out the appropriate contact closure, then the signal from the feedback potentiometer is compared with the control signal at point *A*. When these two signals equalize, the controller opens its output contacts and the motor holds its position.

The flow control signal works in the conventional feedforward manner—linearly with flow. The residual control signal, however, is applied to the rate valve feedback potentiometer and serves to vary the sensitivity of the valve. A large voltage across the potentiometer means the valve does not have to move very far to satisfy its feedback requirements. A lower voltage across the feedback potentiometer means the valve will have to physically move a greater distance (revolutions) in order to satisfy the same required voltage change. Changing the voltage to the feedback potentiometer allows the feed-rate valve to open or close completely independently of the flow signal.

This system has had insufficient field testing to allow any comment on its reliability. However, the advanced technology used in the circuitry makes this system appear to be tailor made for chlorination installations.

*Fischer and Porter.* Their dual signal system is built upon two principal components: (1) a 16-turn Chloromatic valve located within the chlorinator, and (2) a microprocessor-based controller located near the chlorinator for easy operator access.

The Chloromatic valve is a wide-range chlorine feed-rate valve with a characterized plug, which is arranged to accept a single signal input for automatic control. There are 3200 different valve positions in which the valve motor may stop. The schematic arrangement of the dual signal system is shown on Fig. 9-45.

The 53MC microprocessor controller is a single PID loop instrument which can be programmed as a special purpose controller including auxiliary instrument functions that may be part of the control loop.[71] This instrument is based upon a standard PID controller algorithm which can be configured through a built-in side keyboard. It features a modern gas discharge display of process information, both in vertical bar chart form and precise digital displays. Unusual control problems can be solved by using the FAPTRAM programming language. The programmable controller has a pressure sensitive keyboard which contains 13 functional keys used for configuration and programming plus 12 numerical keys for data entry. Three special keys are provided for tuning the constants in the PID loop.

Owing to the grossly oversized venturi meter stated in the field conditions, Fischer and Porter recommend two DP transmitters across the venturi to increase the reliable range. Assuming that reliability of the venturi meter will be acceptable

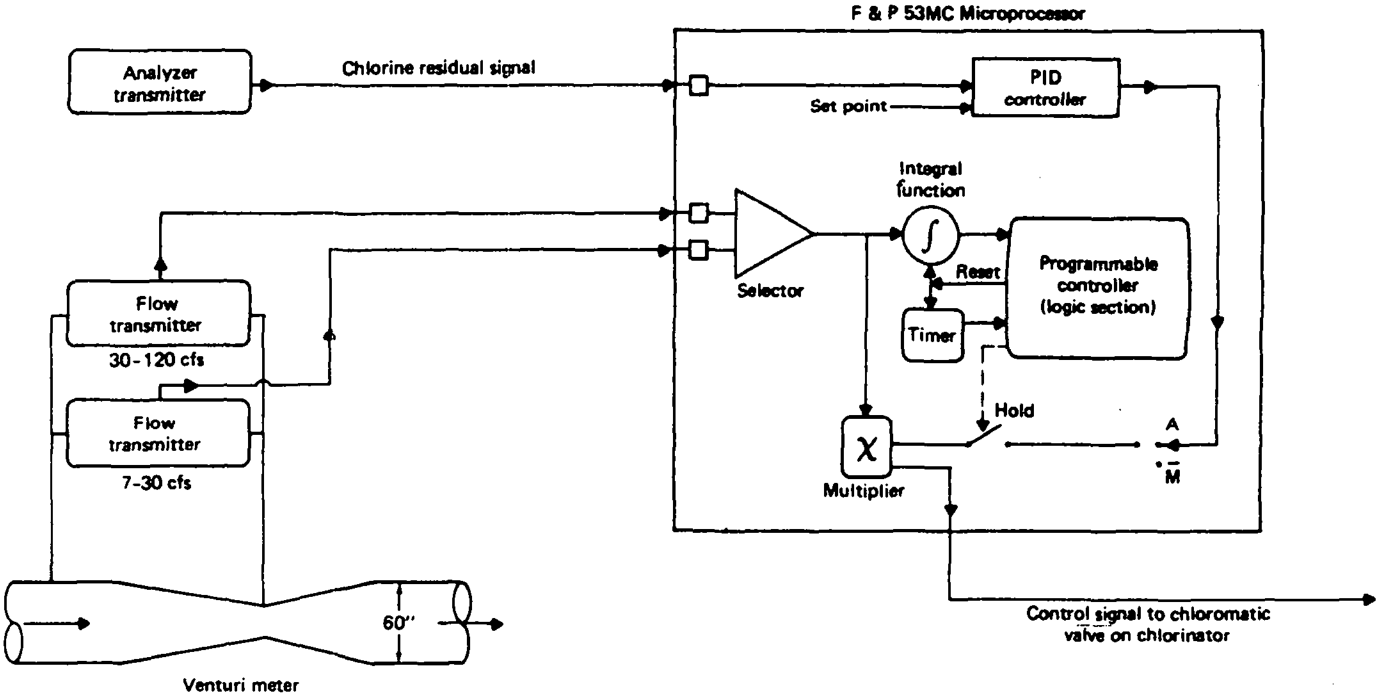


Fig. 9-45. Dual-signal residual control system (courtesy Fischer and Porter Co.).

over a 4 1 range with maximum flow at 120 cfs, the first DP would measure from 120 down to 30 cfs, while the second would pick up at 30 cfs and go down to approximately 7 cfs An accurate flow signal at low flows will greatly improve the quality of the controller program

The two flow inputs and the residual signal serve as the inputs to the controller The analyzer signal is sent to the microprocessor PID controller section This is the feedback loop

The controller selects either flow signal depending upon the flow range and passes it on to be totalized in the integrator section This portion of the microprocessor integrates the water flow over a given period of time, which results in an average flow signal This quantity determines both the frequency and amount of controller correction [72] This provides the solution to the problems that usually occur at low flows.

From the integrator section the signal goes to the programmable controller This segment of the instrument creates a reset signal for both the integrator and the timer The timer is adjustable to control the on time of the controller

Both the residual control signal and the selected flow signal are then sent to the multiplier, which furnish a single output to the Chloromatic valve The multiplier has a built-in ratio station which can be fine tuned at the controller

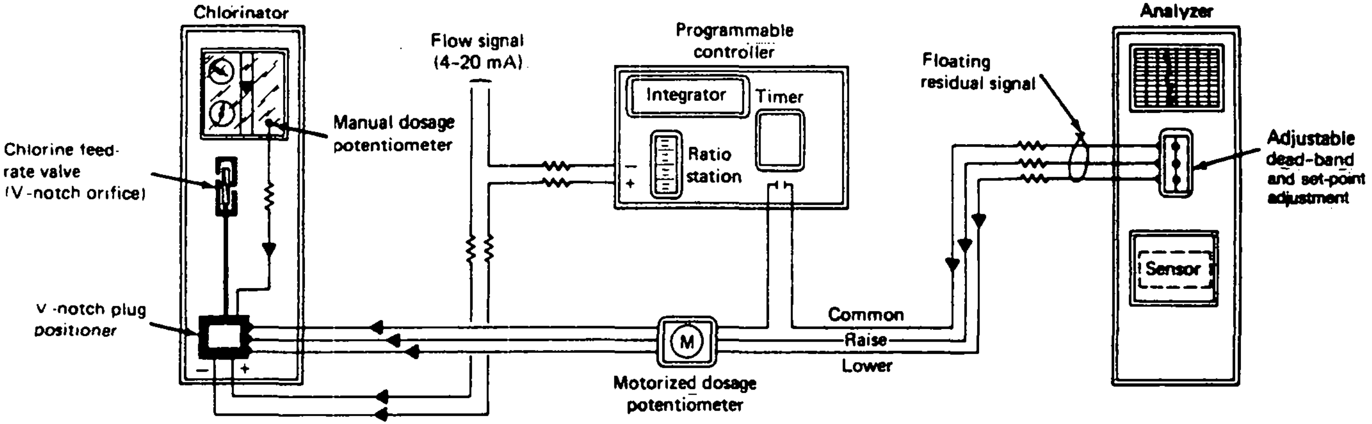
The dosage rate can be called up by the data panel for on-site operator information. The dead band will not exceed one percent, which is beyond detection on the chlorinator rotameter.

The programmable controller provides the operator with the means to fine tune the proportional band gain, the reset action to reduce the error signal, and the derivative action to adjust to rapid rates of change in residual measurements This includes on time for the sample and hold logic and the off or hold time for the logic based upon totalized flow

**Wallace and Tiernan.** Their dual system is based upon the dosage control element in the chlorine feed-rate valve positioner These positioners have always used an adjustable potentiometer to achieve manual dosage control. To achieve automatic dosage control a motor-driven potentiometer is installed in the residual analyzer This 10-turn potentiometer is positioned by a 2-phase reversible motor A residual signal from the high-off-low switch in the analyzer causes the motor to drive the potentiometer in one direction or the other The analyzer provides set point and dead band adjustment These adjustments are one-time set to fit field conditions

The schematic shown in Fig. 9-46 illustrates the operation of this system It is described as a floating control feedback loop The programmable controller integrates the feedforward flow pacing signal with the feedback residual signal

The programmable controller should contain sufficient options to allow the operator to adjust contact closure frequency to fit the system loop time over the process flow range, and to vary closure duration for the same conditions Other options



Notes: The following functions are programmed by the PC for site-specific conditions:
Ratio station: Adjusts chlorine orifice meter span to fit operating flow range.
Integrator: Controls frequency of corrections at higher flows.
Timer: Controls length of all corrections and frequency at lower flows.

Fig. 9-46. Dual-signal residual control system (courtesy Wallace and Tiernan Div. Pennwalt Corp.).

might include the ability to "freeze" the chlorine orifice positioner during a power failure and/or interrupt the chlorine feed-rate during reverse flow conditions.

## INJECTOR SYSTEMS

**General Description.** The power developed by the injector allows the chlorine to flow from the supply containers through the chlorinator, which is the metering system, and then through the injector vacuum line to the injector inlet. At the injector, the chlorine dissolves in the injector water to form a mixture of hypochlorous acid (HOCl) and molecular chlorine ($Cl_2$). This is the chlorine solution which flows in the solution lines to the diffuser at the point of application. This method of feeding chlorine gas is unique to water treatment processes (potable water, wastewater, and industrial waters). In the beginning, chlorinators metered and controlled directly into the process flow This practice proved to be impractical over the long term. There were and are some exceptions. The difficulties with the direct feed system resulted from feed-rate sensitivity due to ambient temperature changes and low solubility of chlorine in water at atmospheric pressure. The vacuum system invented by G F Wallace overcame these difficulties and provided several advantages:

1 It is the easiest method of dissolving chlorine in water.

2 Chlorine is easily handled when in solution.

3 Since the injector creates a vacuum, it allows chlorine to be metered under a vacuum. This is the most accurate way of metering, since constant density is maintained and is not affected by ambient temperature changes.

4 Operation under a vacuum is safer than operating under pressure.

5 A metering system can be easily designed to stop automatically if the vacuum should fail.

6 Available vacuum can be used for automatic switchover of containers.

7 Injector vacuum level can be used to provide two alarm signals: (1) loss of chlorine supply, (2) injector malfunction or loss of water pressure.

8 Injector vacuum can be used to generate a variable chlorine feed rate as a function of chlorine residual (compound loop control).

**System Description.** The injector system is the heart of the entire chlorination facility If this system is inoperable, no other part of the system can function. The various parts of this system include: (1) the operating water supply to the injector; (2) the injector; (3) the injector vacuum line from the chlorinator; (4) the injector discharge system, described as the chlorine solution line; and (5) the diffuser at the point of application

### Operating Water Supply:

*Water Quantity* Injectors are designed to develop about 25 in. Hg vacuum at the injector inlet when the chlorinator is at maximum chlorine feed rate and the

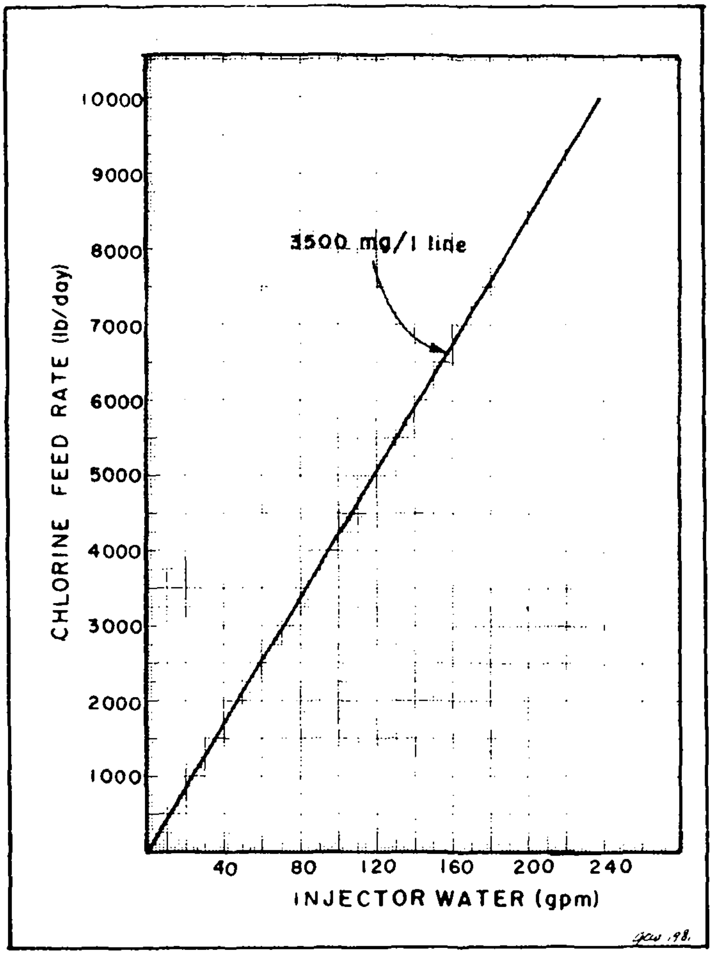


Fig. 9-47 Injector chlorine solution curve for limiting chlorine concentration of 3500 mg/L

chlorine solution is discharging at atmospheric pressure, i.e., no back-pressure The water flow through the injector must be sufficient to limit the chlorine solution strength to 3500 mg/l Above this strength molecular chlorine appears in significant amounts, which breaks out of solution causing off-gassing at the point of application if open to the atmosphere, and gas binding in solution lines under low negative heads (see Table 4 1) Either condition is intolerable Fig 9-47 shows the minimum amount of water required to limit the chlorine solution to a maximum strength of 3500 mg/l for various gas flow rates A rule of thumb is approx 40 gal water lb/day chlorine, more or less depending upon local conditions

*Water Pressure vs. Back-Pressure.* A second factor is the pressure at the point of application of the chlorine. This is known as injector back-pressure. A higher back-pressure requires a higher injector inlet pressure and more operating water to make the injector function properly. The injector also has minimum operating water requirements. Chlorination equipment manufacturers use injector operating curves that specify how much water at which pressure is required for a given amount of chlorine to be applied against a given back-pressure. It is the designer's responsibility to make a hydraulic analysis of the chlorine solution line between the injector and the point of application to establish the amount of back-pressure to be expected. With this information and the maximum chlorine feed rate desired, the chlorinator manufacturer can then advise the necessary water supply inlet pressure required at the injector and the optimum injector operating water quantity. The back pressure should never be allowed tọ drop below 2 psi.

In spite of manufacturers' injector curves it is unwise to operate any injector on less than 50 psi inlet pressure unless there are extenuating circumstances.

*Flow Meters.* Injectors are usually available in four sizes: 1" fixed-throat type, 2", 3", and 4" adjustable-throat type. The fixed-throat injector assembly utilizes interchangeable throats and tailways with various-size openings for different conditions of chlorine feed rate and hydraulic conditions (back-pressure). Therefore the water flow through a fixed-throat injector is predictable. This is not the case with the adjustable-throat injector. For this reason, when adjustable-throat injectors are used, it is mandatory that the operator be provided with an indicating flow meter (for each injector) with a 3 to 1 operating range and a head loss at maximum flow not to exceed 5–6 ft.

*Pressure-Regulating Valves.* In cases where more than ample pressure is available to operate the chlorinator there is no need to use pressure-regulating valves upstream from the injector except in cases of abnormally high pressure—that is, > 150 psi.* The reason for not requiring pressure-reducing valves is the hydraulic characteristics of an injector. It will consume all of the pressure available on the upstream side of the injector.

## Hydraulic Gradient Analysis:

*General Discussion.* It is necessary to consult manufacturers' injector efficiency curves to determine injector operating water pressure and quantity. The reader is cautioned that some manufacturers may have different sets of curves for different modes of vacuum operation, i.e., remote vacuum, variable vacuum control, and/or sonic flow vs. non-sonic flow. Whenever the chlorinator feed rate is varied via the differential vacuum regulator, higher internal operating vacuum levels must

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* The exception is when booster pumps are used or where cavitation of the injector tailway occurs.

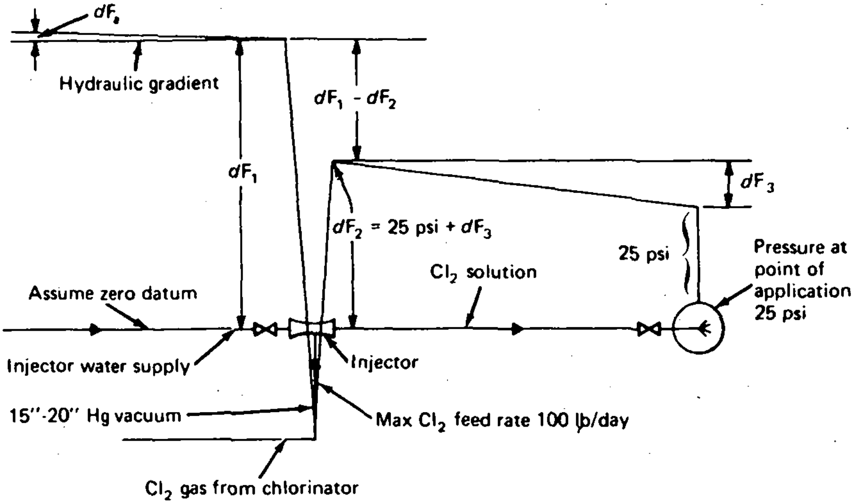

Fig. 9-48. Typical injector hydraulics, where $dF_a$ = friction loss in injector water supply line to the injector; $dF_1$ = required operating pressure (consult manufacturer's curves); $dF_1$–$dF_2$ = pressure drop across injector required for satisfactory operation; $dF_3$ = friction loss in chlorine solution line from injector to point of application. The chlorinator injector "back pressure" is $dF_2$. $dF_1$ is also dependent on the amount of chlorine to be injected as well as on control mode, i.e., use of variable orifice positioner or differential regulator.

be used; therefore the injector requires more power, and hence more water pressure for the same back-pressure. This is the case with the Wallace and Tiernan compound loop control system shown in Fig. 9-42. When remote vacuum is used injector vacuum levels need to be increased about 5 in. $H_2O$.

Injectors can be installed in either the vertical or horizontal position. The only precaution required is to change the position of the check valve inlet block on the 3" and 4" injectors so that the ball-check will operate as it does in the vertical position.

Figure 9-48 is a typical injector hydrualic gradient diagram where $dF_1$ = IOP = injector operating water pressure, $dF_2$ = BP = injector back-pressure, or hydraulic gradient immediately downstream from the injector (outlet of tailway). Injector water quantity $Q$ is dependent upon three factors: (1) maximum chlorine gas feed rate; (2) size of injector; (3) back-pressure. However if the water pressure available to operate the injector is greater than required by the gradient analysis shown in Fig. 9-48, this water pressure will determine the amount of injector operating water for the case of the one-inch fixed-throat injectors. The throat size adjustment provided for in the 2-, 3-, and 4-inch injectors allows the operator to adjust the inlet water flow to conform to the hydraulic gradient analysis.

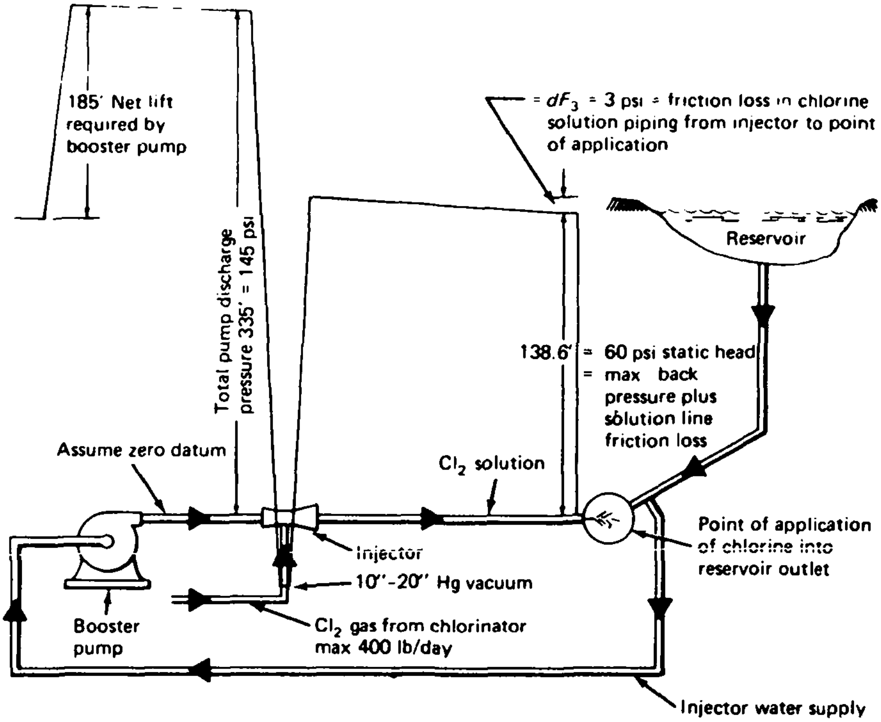

Fig. 9-49. Hydraulic gradient injector system. Chlorine feed rate = 400 lb/day. Manufacturer's injector curves for this feed rate at 65 psi back pressure requires minimum injector water $Q = 20$ gpm. For the pump, the following amounts are practical in terms of safety factors: $Q = 40$ gpm for a turbine and $Q = 25$ gpm for a centrifugal.

*Example I.* Fig. 9-49 illustrates the hydraulic gradient of the injector system described as follows:

Water is to be chlorinated at the outlet of an impounding reservoir. The location of the equipment will be such that the maximum static head at this point is 140 ft (60 psi). This then is the maximum back pressure at any time. The peak water flow to be treated is estimated at two and a half times the average daily consumption of 4 mgd = 10 mgd. Chlorine demand tests show that during summer months the demand is as high as 2.8 mg/l. Therefore the chlorinator should be sized to feed at least 4 mg/l in order to provide an adequate free chlorine residual. The capacity of the chlorinator must be 4 mg/l × 8.33 lb/mg × 10 mgd = 330 lb/day. The selection would be a chlorinator with a maximum capacity of 400 lb/day—one of the breaking points on overall size of chlorinators. Consultation with the manufacturers' injector curves reveals that a fixed throat injector will be used and that the most efficient size for feeding 330 lb/day maximum versus a 60 psi back-pressure will require an inlet pressure of 155 psi, which will produce a flow through the injector, $Q = 20$ gpm. Therefore select a booster pump with $95 \times 231 = 220$ ft total net head lift and $Q$ of 20 gpm plus a 25 percent (25 gpm) safety factor if the pump is to be centrifugal or 100 percent (40 gpm) if it is to be a turbine type. Additional allowance for friction loss in the solution line should be added to the pressure at the point of application. Assume that the solution line has an equivalent length of 150 ft. A chlorine solution flow of 20 gpm* in a 1½" pipe will have a pressure drop of 4 ft per hundred. This will then raise the downstream back-pressure to approximately 63 psi. Since the pump chosen should have some factor of safety, we will select a pump to deliver 40 gpm at a total net head of 250 ft for a turbine and 25 gpm at a total net head of 250 ft for a centrifugal. Because of the high head, a turbine pump is preferred in this instance.

*Example II.* Installations in which the point of application is below the injector require that the chlorine solution be sized so as to provide an artificial back-pressure of approximately 2 psi just downstream from the injector. This example involves a 2000 lb/day chlorinator using a 2" adjustable throat injector. The point of application is 25 ft below the injector, and the water surface is 15 ft below the injector. Therefore the static back-pressure is −15 ft. The minimum amount of injector water will be 50 gpm. In negative head situations, there will be greater opportunity for developing chlorine fumes at the point of application owing to breakout of molecular chlorine under a negative pressure. Therefore add 15 percent to the injector water flow to decrease the chlorine concentration—try 65 gpm. The injector curves indicate a requirement of 25 psi with a back-pressure of 2 psi to meter 2000 lb chlorine per day.

Next choose a chlorine solution line small enough to produce 2 psi back pressure at the outlet of the injector. See Fig. 9-50 for the hydraulic gradient. Analysis of the solution line shows an equivalent length of 96 ft. Therefore choose a 2" pipe size. At 65 gpm the friction loss in 96 ft of pipe is approximately 12 ft. Therefore provide a diffuser with an 8 ft head loss. The total loss of 20 ft meets the requirement to provide a 2 psi back-pressure at the injector to prevent fuming at the diffuser. In all cases diffuser head losses of 8–10 ft are highly desirable because of the jet velocity attainable. This results in superior initial mixing. (See Chapter 8.)

**Remote Injectors.** Installation of injectors remote from the chlorinator location is more the rule than the exception. This is especially true in the wastewater application, which has already been described in Chapter 8. In potable water treatment there are two major advantages in having the injector adjacent to the diffuser: (1) it shortens the loop time in residual control application because gas velocities five times that of chlorine solution velocities can be tolerated; and (2) head-loss inherent in solution lines can be transferred and added to the diffuser loss to provide better mixing. See the "Diffuser" section this chapter.

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* The flow through the injector is limited by the discharge pressure of the pump. In the case of the turbine pump the excess flow recirculates in the by-pass. (See Fig. 9-52.)

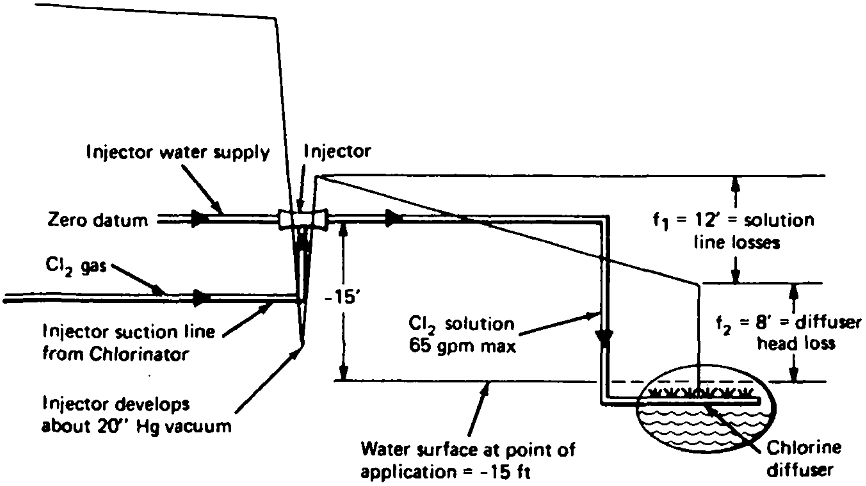

Fig. 9-50. Hydraulic gradient of injector system to prevent negative head at the diffuser.

**Vacuum Line Design.** The design of a long vacuum line (> 100 ft) should include the following features. The vacuum line (regardless of length) between the chlorinator and the injector should be sized so that the total pressure drop in this line is not more than one and one-half in. Hg. A shutoff valve should be provided at each end of this vacuum line. A vacuum gage should be installed adjacent to, but downstream from, the shutoff valve at the injector end. The injector should always be installed in a horizontal position to achieve a low profile (better hydraulics) and to allow easy disassembly of the injector.

The optimum pipe size for vacuum lines between the metering equipment (chlorinators or sulfonators) and the injector is subject to a great deal of scrutiny. White has investigated the hydraulic characteristics of three remote injector systems varying in distances from 750 to 8740 ft. The most comprehensive study was of a chlorination system with 3–2000 lb/day chlorinators remotely located from a single 3-in. injector connected by one 3-in. PVC vacuum line 8740 ft long.[25] Friction loss data were plotted showing the friction loss factor $f$ as a function of Reynolds Number, $N_r$ (see Fig. 8, Appendix). The response time (lag time) between the chlorinators and the injector was determined by 30-sec. interval amperometric titrations of the chlorinated effluent immediately downstream from the chlorine diffuser, which was within 25 ft of the injector. As a check on these field observations Fischer and Porter Co. Engineering Department set up a laboratory experiment using a 400 ft ¾-in. vacuum line to a remote injector and a variable chlorine feed rate of 150–500 lb/day. The results of this experiment when extrapolated agreed closely with the field results by White and Stone described above.[25]

Several important conclusions were drawn from these observations: 1) for any given system the lag time appears to be almost constant regardless of magnitude of change of the gas feed rate; 2) the higher the vacuum level in the vacuum line the shorter the lag time because the lower density of the gas provides a higher velocity; 3) lag time is independent of total volume of the vacuum line; 4) friction factor *f* varies significantly with Reynolds Number (see Fig. 8 Appendix); and 5) when the total pressure drop is greater than about 1.5 in. Hg there is a noticeable decay in the vacuum level of the entire line (see Fig. 9-51). Referring to this figure, the total pressure drop was about 1.5 in. Hg at flows less than 500 lb/day. Above this flow (i.e., 500–5500 lb/day), the pressure drop was practically constant. It varied from 2.88–3.06 in. of Hg, while the vacuum level varied from 5.25 to 22.25 in. Hg. Over this range of vacuum level and at a constant temperature of 68°F the density of gas varied from 1.55 lb/ft$^3$ at the low vacuum to 0.048 lb/ft$^3$ at the high vacuum—this is a range of 32–1. From these values it is obvious that the flow conditions of this vacuum line are highly unstable. The instability of this sytem is a result of the high-total pressure drop.

These observations bring up the question of the design procedure for an optimum size vacuum line for a given length and amount of gas flow. It would seem prudent to design for the severest conditions. Instead of designing for the minimum vacuum

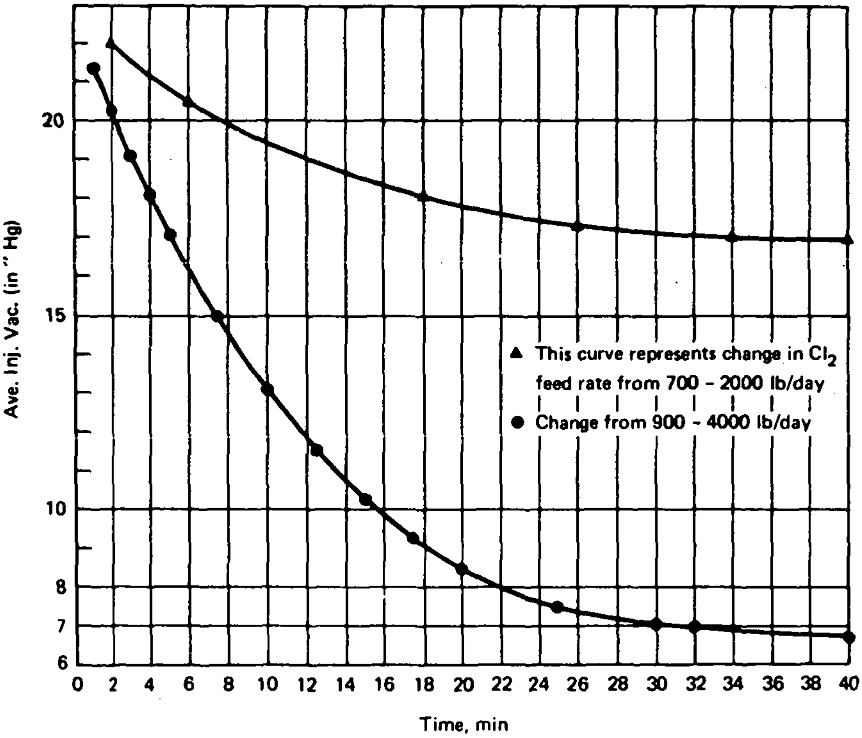

Fig. 9-51 Vacuum level decay in long vacuum lines due to excessive friction loss.

conditions allowable for the proper operation of chlorinators and sulfonators (about 8–10 in. Hg), the maximum injector vacuum level should be assumed (22–23 in. Hg). At this level the *total* pressure drop in the system, regardless of pipe length, should be limited to 1.50–1.75 in. Hg. One such system designed to include these factors has been in operation long enough to draw the following conclusion: it is a stable system with rapid response and therefore close to the optimum design. The maximum vacuum decay level from minimum to maximum feed rate is only about 3 in. Hg (i.e., from 24–21 in. Hg, vacuum).

The design procedure is to first choose a line size. This particular case was for a dechlorination system—3300 ft from sulfonator to injector, 8000 lb/day maximum feed rate. Let us try a 4-in. Sch 80 PVC pipe, $d = 3.826$ in. Using the following equation corrected to pressure drop in inches of Hg:

$$\Delta P = \frac{11.89 \times L \times f \times W^2}{10^9 \times \rho \times d^5} \qquad (9\text{–}11)$$

where

$\Delta P$ = total pressure drop, in. Hg
$L$ = length of line in ft
$f$ = friction factor from Fig. 8, Appendix
$W$ = lb/day $Cl_2$ or $SO_2$
$\rho$ = density of gas, lb/ft$^3$*
$d$ = inside pipe diameter, in.

To find $f$ from Fig. 8, Appendix, it is necessary to calculate the Reynolds Number of the system:

$$N_r = \frac{6.32 \times \omega}{\mu \times d} \qquad (9\text{–}12)$$

where

$\omega$ = lb/hr gas flow
$\mu$ = viscosity of gas in cp*
$d$ = inside pipe diameter in in.

$$N = \frac{6.32 \times 8000}{0.0133 \times 3.826 \times 24}$$

$$N = 41{,}399$$

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* For gas density values, see Fig. 2, Appendix.

* For gas viscosity values see Fig. 3, Appendix.

So from Fig. 8, Appendix,

$$f = 0.027; \therefore \Delta P = \frac{11.89 \times 3300 \times 0.027 \times (8000)^2}{10^9 \times .05 \times (3.826)^5}$$

$$\rho = 0.05 \text{ lb/ft}^3 \text{ at 22 in. Hg. vac. and } 68°\text{F}.$$

*Answer:* $\Delta P$ = 1.65 in. Hg.

At 6000 lb/day flow $\Delta P$ is about 0.16 in. Hg. Now to calculate the lag time in this system it would be appropriate to calculate it for 4000 lb/day gas flow, but at 25 in. Hg vacuum. So 4000 lb/day is 0.05 lb/sec. The gas density at 25 in. Hg vacuum and 68°F is 0.03 lb/ft³ so;

$$Q = \frac{0.05 \text{ lb/sec}}{0.03 \text{ lb/ft}^3} = 1.54 \text{ cfs}$$

$$V = \frac{1.54}{0.07986} = 19.32 \text{ ft/sec}$$

Therefore, the lag time for any change in gas feed rate is on the order of 3 min. To show that the lag time would be nearly the same at 8000 lb/day assuming a 22 in. Hg vacuum level, 8000 lb/day = 0.09 lb/sec and the density = 0.048.

$$Q = \frac{0.09 \text{ lb/sec}}{0.048 \text{ lb/ft}^3} = 1.88 \text{ cfs}$$

$$V = \frac{1.88}{0.07986} = 23.54 \text{ ft/sec}$$

So at double the gas flow the lag time decreased to about 2.35 min. Therefore, as the flow of gas changes, the density changes in a direction which provides an almost constant system lag time regardless of flow change.

It is to be noted that the physical properties of chlorine and sulfur dioxide gas under a vacuum are so similar that calculations for either are interchangeable; so for simplicity, long vacuum lines can be designed for either gas based on the physical characteristics of chlorine.

## Booster Pumps:

*Turbine vs. Centrifugal.* Chlorinator or injector water booster pumps are as important as the injector or the chlorinator. If the booster pump is not large enough, the chlorinator will not operate. Therefore never undersize or try to economize while attempting to select a pump. If anything, oversize. It is always a good idea

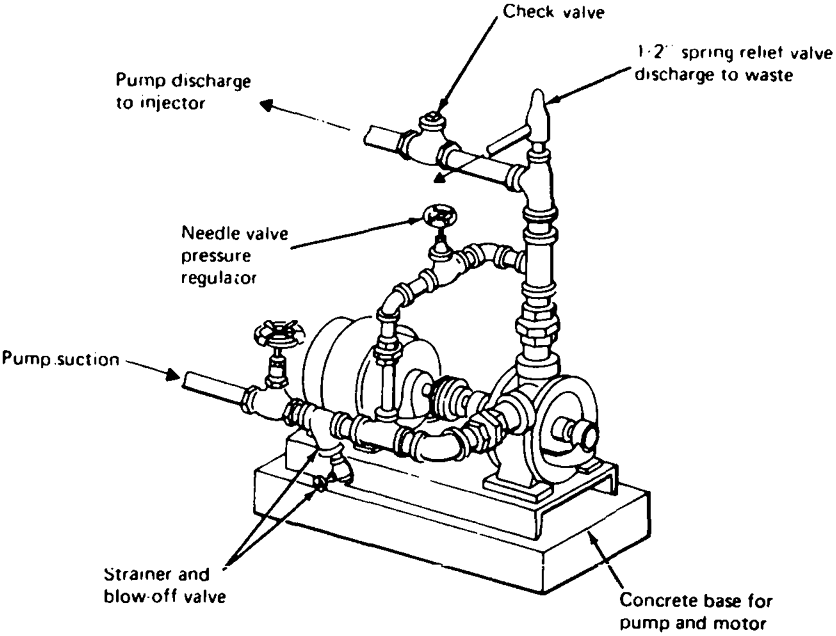

Fig. 9-52. Turbine type booster pump showing by-pass piping. (courtesy Wallace and Tiernan Div. Pennwalt Corp.).

to add 10 percent to the estimated back pressure, and be sure that the amount of chlorine to be fed is a little more than calculated.

Estimating the injector operating water depends on whether the pump to be used is a centrifugal or a turbine.

If the pump selected is a centrifugal, it will make a difference whether it is a unibuilt type or has an outboard bearing. If it is the latter, a higher wear factor for *Q* is allowable than if it is unibuilt. Picking a *Q* in excess of 15 percent of what the fixed throat injector will pass at the discharge pressure of the pump will overload the motor thrust bearing and cause undue wear. A centrifugal pump with an outboard bearing can easily handle the injector *Q* plus 25 percent. With adjustable throat injectors this is not a problem, because the injector *Q* is easily adjusted in the field.

A turbine pump, which is usually the one of choice for all fixed injector throat chlorinators, should be arranged with an adjustable pressure bypass assembly, as shown in Fig. 9-52. In these cases, the pump is selected to deliver 2 *Q*. In other words, if the injector requirement is 3 gpm, select a pump to deliver 6 gpm. The regulating bypass assembly allows the excess water to flow back into the suction. This is done by the needle valve in the bypass. As the pump wears over a period of time, and the pressure drops off, the bypass is closed off more to compensate for this wear.

With water that has a quantity of sand, it is more desirable to use a centrifugal pump, because sand will ruin a turbine pump in a very short time.

Most of the chlorinator booster pump installations require a turbine pump because of high head and low $Q$ requirements. For example, all chlorinators in the capacity range of 3 to 400 lb/day use a fixed throat injector. The largest fixed throat injector will pass about 22 gpm. Most injector water requirements are for less than 15 gpm.

Centrifugal pump selection usually begins when the injector operating water approaches 15 gpm.

*High Back-Pressure Conditions.* There are situations of high static pressures that are beyond the ability of high-head multistage 3500 rpm turbine pumps and or high-head centrifugal pumps. When conditions exist that are beyond the capabilities of these pumps, the chlorine solution has to be pumped. It is fair to say that the upper limit for a conventional turbine pump application would be a condition for a fixed-throat injector where the maximum chlorine feed rate is 400 lb/day and the maximum back-pressure 140 psi. When the chlorine feed rate and back-pressure combination exceeds 100 lb/day and 75 psi, respectively, pumping chlorine solution should be investigated. When a 2-inch injector is required, pumping chlorine solution should be investigated when the combination of chlorine feed rate and back-pressure is 1000 lb/day and 60 psi, respectively. For 3-inch and 4-inch injectors the chlorine solution should be pumped when the back-pressure reaches 15–20 psi.

When it becomes necessary to pump the chlorine solution the pump system should be arranged as shown in Fig. 9-53. The two basic requirements for this system are: (1) the regulating valve should be adjusted so that there is always approximately 2–5 psi back-pressure on the injector (a negative head must be avoided); and (2) the pump should be sized to deliver the required injector water plus an additional 30–40 percent dilution water.

This system operates on the principal that the spring-loaded regulating valve creates a pressure drop when the pump is operating. The pressure on the downstream side of this valve becomes the injector "back-pressure." Therefore the pressure drop across the regulating valve plus the friction loss in the system equals the TDH* requirement of the pump. If the chlorinator utilizes a fixed-throat injector, the largest-size throat should be used so as to insure minimum chlorine solution concentration.

Two types of pumps are available for this service. The type that has been in service for the longest time for pumping chlorine solution is the titanium pump line of the Duriron Co.[25] The City of San Francisco Water Dept. has reported excellent service by these pumps for more than 20 years. In recent years the Duriron

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* TDH = total dynamic head.

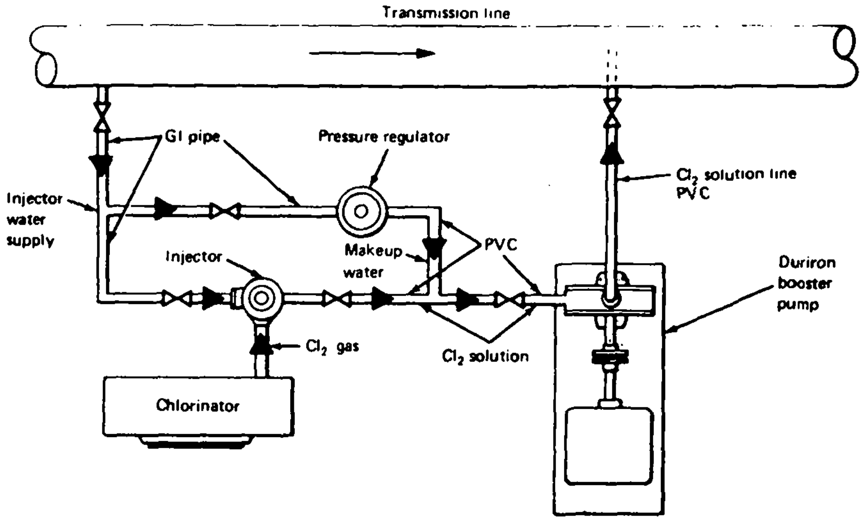

Fig. 9-53. Schematic arrangement showing booster pump downstream of injector. All pipe and valves downstream of injector and pressure regulator must be corrosion resistant, i.e., PVC, rubber-lined steel, Saran-lined steel, or fiber glass.

Co. has made a line of reinforced Fiberglas pumps for this service.[27] The Fybroc Division of the Met Pro Corporation also have a line of Fiberglas pumps available for this service.[28]

*Example.* Assume a transmission line with a maximum static head of 150 psi and a chlorine requirement of 1000 lb/day. Using Wallace and Tiernan Injector Performance Curve 25.100.190.021 shows that the best a 2-inch injector can do with 150 psi initial water pressure is 80 psi back-pressure at 80 gpm. Therefore the chlorine solution pump must be able to boost 80 gpm injector water plus about 25 gpm makeup water to 155 psi plus 10 psi friction loss or 165 psi. So $165 - 80 = 85$ psi × $2.31 = 196$ ft TDH. This situation calls for a pump to deliver 105–110 gpm at a TDH of 205–210 ft.

**Designers Check List for Injector System.** The injector system and chlorine solution lines usually include all of the following components:

1. Injector water-pressure gage
2. Injector vacuum gage for remote injector installations
3. Injector vacuum line shut-off valve at remote injector loction
4. Chlorine solution pressure gage located immediately downstream from the injector to indicate injector back-pressure (not required on fixed throat injector installations)
5 Injector water-pressure switch for low-water-pressure alarm

6. Injector water flow meters for multiple chlorinator installations of chlorinators using 2", 3", and 4" injectors
7. Chlorinator–sulfonator built-in vacuum switch and alarm for both high and low vacuum
8. Compound back-pressure gage for injector discharge

## CHLORINATION STATIONS

**Principal Considerations.** The design and layout of any chlorination station must be based upon the following considerations:

1. Chlorine container selection
2. Chlorinator capacity
3. Points of application
4. Injector requirement
5. Methods of control
6. Alarms
7. Safety equipment
8. Chlorine residual testing facility
9. Chlorine storage inventory system
10. Housing requirements—space, ventilation, lighting, and heating
11. Reliability provisions

All of these items are addressed in detail elsewhere in this text.

**Individual Deep-Well Station.** This is probably the most widely used type of chlorinator station. The chlorine may be applied either down the well or at the well pump discharge. Fig. 9-54 shows the application down the well. Whenever possible, this is the preferred method for a variety of reasons.

1. No injector booster pump is required.
2. Chlorine solution lines may be used simultaneously to feed a sequestering agent to prevent deposition of iron or manganese in the distribution system.
3. Chlorine solution line provides means for intermittent purging and cleaning of aquifier with heavy doses of chlorine.
4. It provides longer contact time.

Special attention should be given to the point of application and the injector hydraulics. The chlorine solution line must terminate at least ten feet below the pump bowls; the chlorine solution strength should be limited to about 100 ppm; and the alkalinity of the water should be at least 100 ppm.[29] These factors prevent chlorine corrosion of the pump and well casing.

The injector water line must be taken off the pump discharge line downstream from the check valve. Therefore, when the pump shuts down, the pipeline from the check valve drains back into the well casing. This creates a negative head on

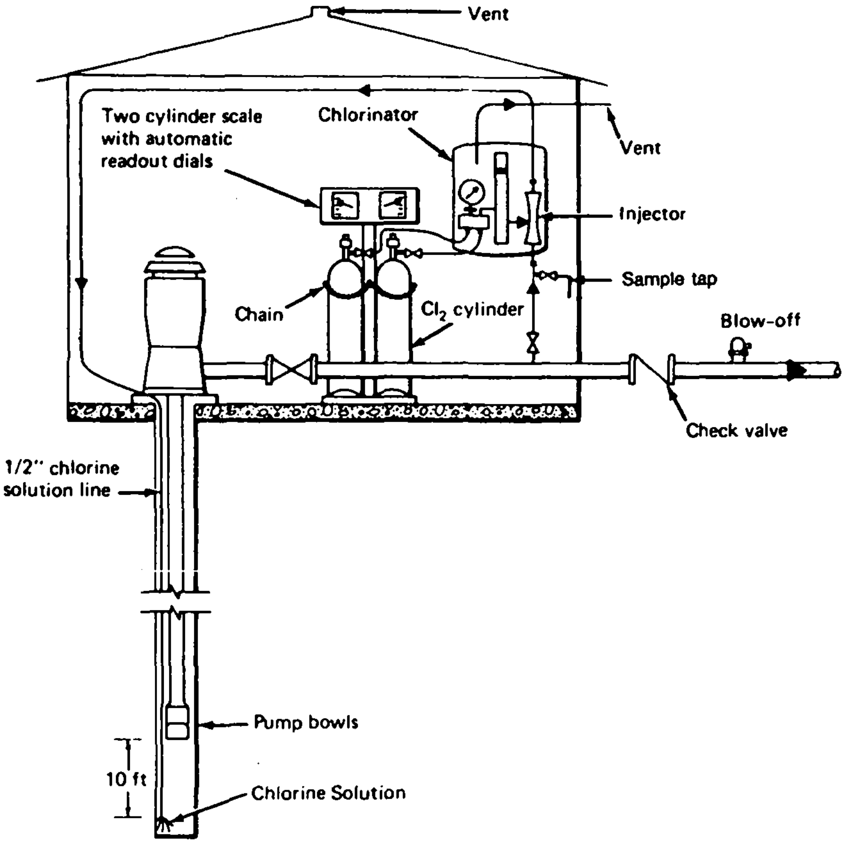

Fig. 9-54. Typical chlorinator installation with chlorine applied down well.

the upstream side of the injector, which soon equalizes to become the same as the negative head in the chlorine solution line. This equalizing of negative head on both sides of the injector allows the chlorinator to automatically shut down without any siphon action from the chlorine solution line. If the injector water line is taken off downstream from the pump discharge check valve, the chlorinator will continue to operate regardless of the well pump. Putting a solenoid valve in the injector water line at this point is useless, because the chlorinator would continue to operate without injector water, owing to the siphon action of the negative head on the chlorine solution line.

When it is not convenient to put the solution line down the well the alternative method is to utilize a chlorinator injector booster pump and apply the chlorine at the well discharge, as shown in Fig. 9-55. In this case the booster pump suction and the chlorine solution discharge must be downstream from the well pump check valve. Then, when the well pump shuts down, the injector pump also shuts

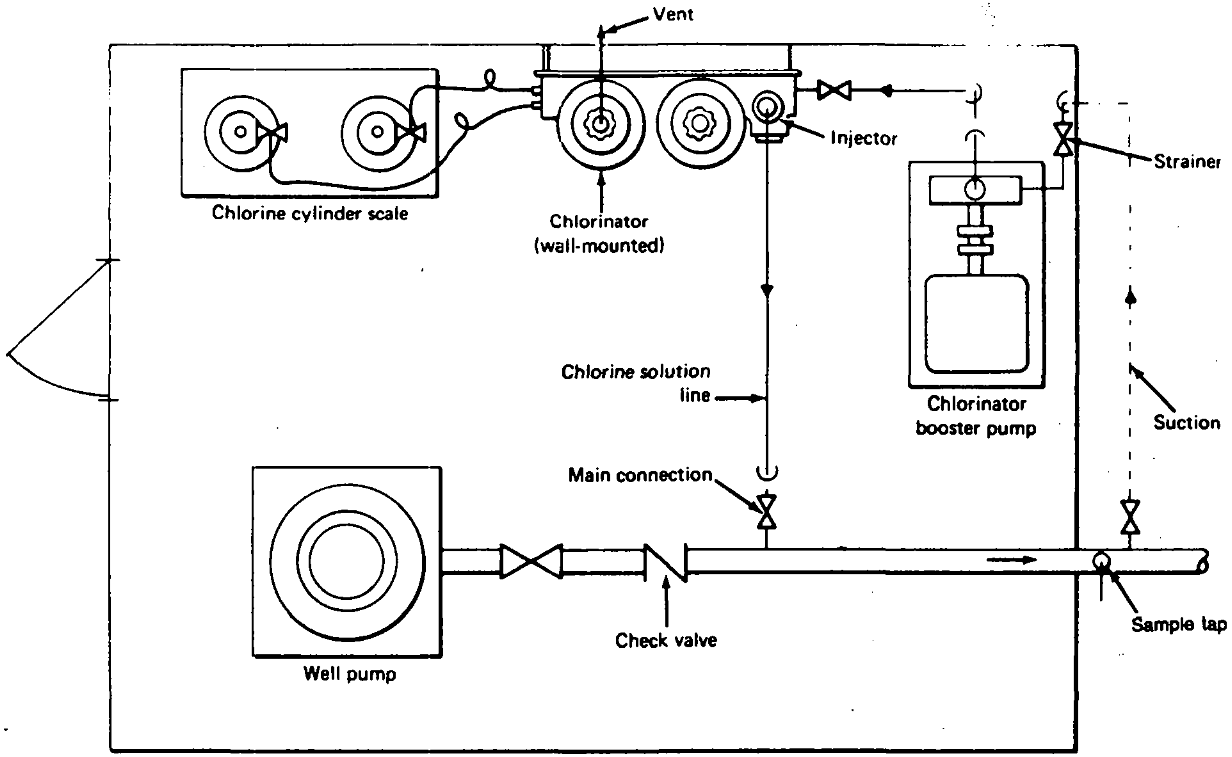

Fig. 9-55. Typical chlorinator installation with point of application in well pump discharge.

down and the pressure on both sides of the injector equalizes, thereby automatically stopping the chlorinator This is known as semiautomatic operation

**Multiple-Well or -Pump Stations.** If there is more than one well station discharging into a common line, it is often preferable to use one chlorinator and one point of application in the common well discharge line. For such a situation the chlorinator control could be either flow-proportional from a primary flow meter or step-rate from an adjustable-rate controller.

For purposes of illustration, the method of step-rate control will be used. This method is practical at a pumping station when the pump controls are at one location or near one another. For widely scattered well stations, the electrical wiring becomes expensive and cumbersome. Fig. 9-56 shows a schematic of a pump station with three pumps of different capacities arranged to provide a separate rate of chlorination for the various combinations of pumps. The usefulness of step-rate control diminishes as the number of rates exceeds four or five, simply because the electrical interlocking gets overly complicated. However, if a primary metering device is not going to be provided at a multiple-pump station, the only method that can be used for chlorinator pacing is the step-rate type. With this in mind, the designer should select pumps of similar capacities, so that the control is limited to only four or five rates.

**Relay Stations and Transmission Lines.** Probably the only simple manual control chlorination stations are those which treat a constant flow of water that is being transferred from one reservoir system to another, with no user takeoffs between. These examples of constant flow are hydraulic rarities. There is usually some fluctuation in flow worth accounting for, particularly if the objective of chlorination is to provide a chlorine residual in the entire transmission line for purposes of maintaining the "C" factor or water quality control.

When it is necessary to maintain chlorine residuals in a distribution system, relay stations are often used. Because of problems of logistics, it is not necessarily convenient to install a primary metering device to pace the chlorinator; it is generally more desirable to rely entirely on straight residual control. The schematic for such a system is shown in Fig. 9-41 and 9-57. The key to a successful direct residual control system is to design a short loop time, 60–90 sec. at average flow, and utilize the chlorinator injector pump to supply the sample to the residual analyzer. Both the chlorine solution diffuser and sample take-off should incorporate the design principles described for Fig. 9-41 and 9-57.

This method is suitable if the flow changes in the distribution system reflect the usual diurnal domestic consumption. The chlorine residual controller can react fast enough to keep up with these fluctuations. Such a control cannot be used alone if the change in flow is abrupt, as reflected in a step-rate change caused by a nearby pumping station.

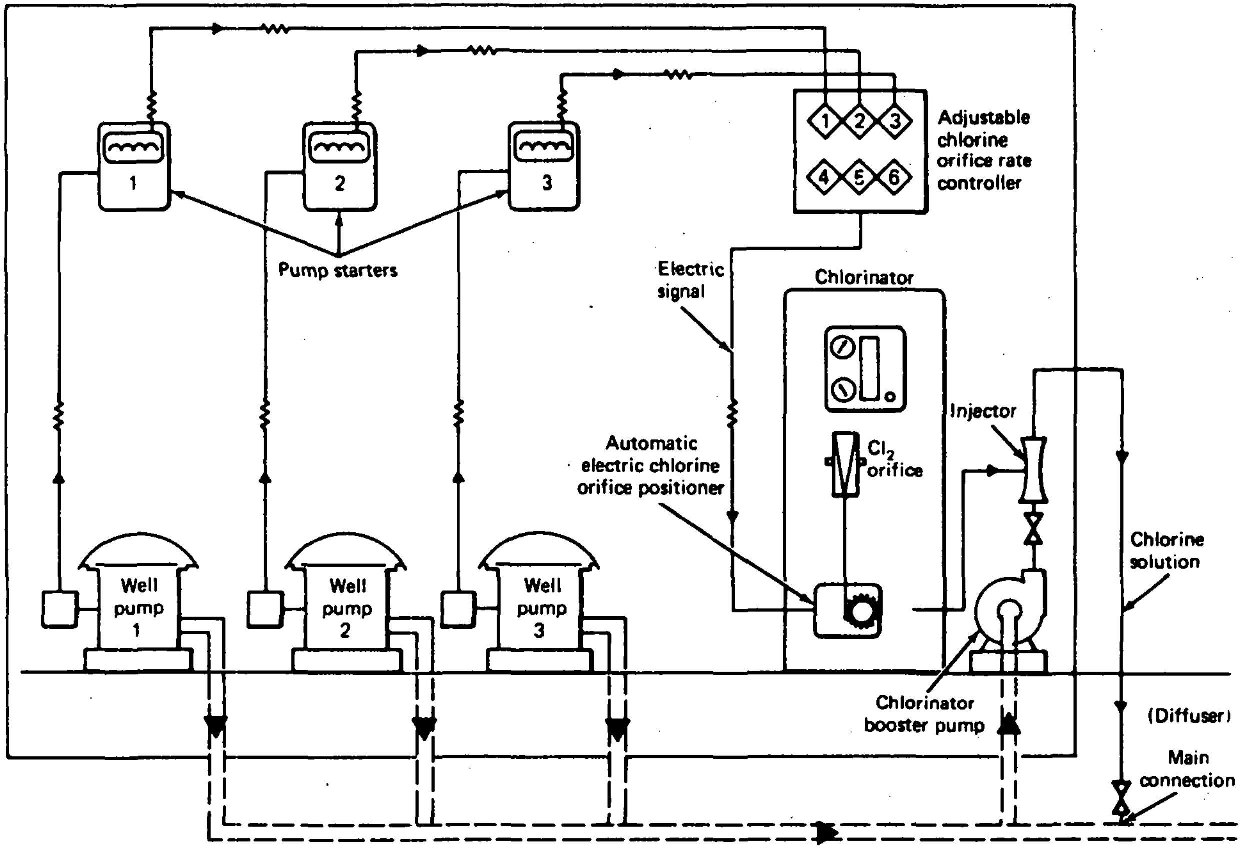

Fig. 9-56. Typical step-rate control utilizing electrically operated chlorine orifice positioner

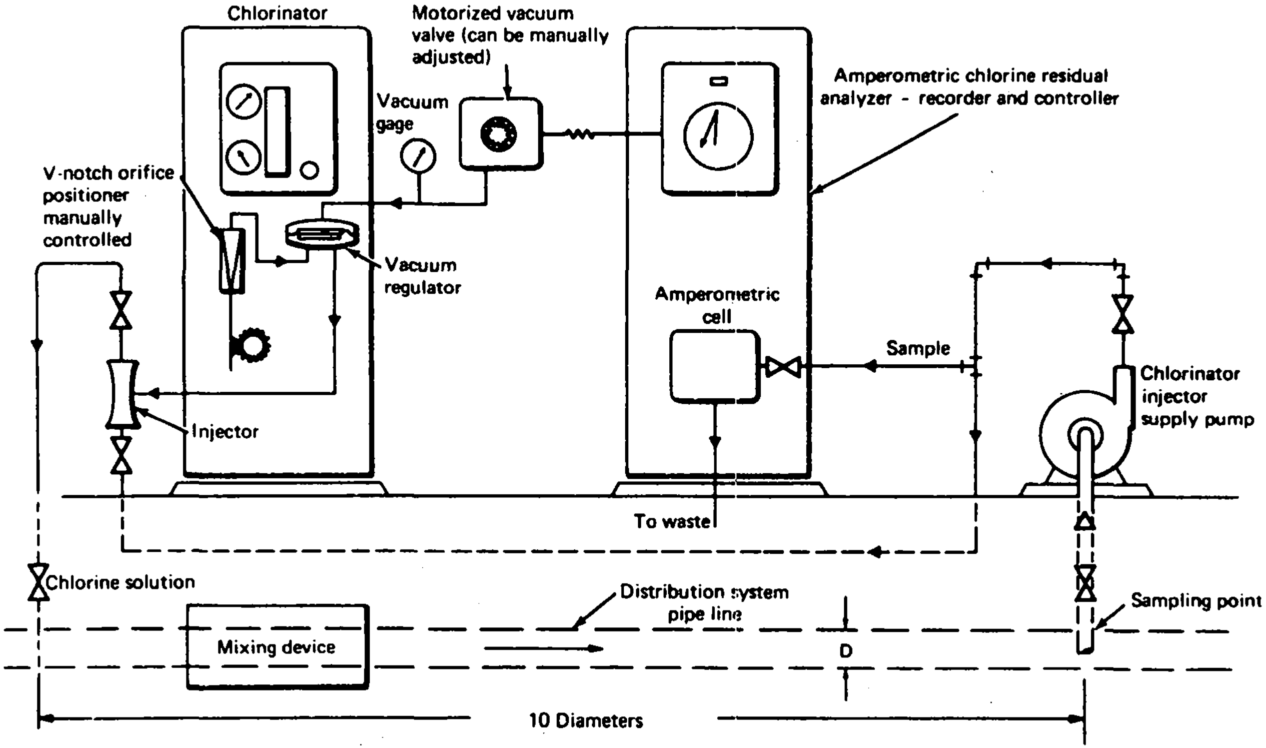

Fig. 9-57 Distribution system relay station with direct residual control. See also Fig. 9-41

## Reservoir Outlets:

*General Discussion.* It is common engineering practice in distribution system design to use balancing reservoirs that float on the distribution system hydraulic gradient. This is a convenient way to balance the flow in a large system. It also helps to solve the problem of pressure equalization by using reservoirs as pressure breaks in hilly terrain. The flow into and out of these reservoirs is almost always by a common pipe. Reversal of flow does occur in many of these systems where the outflow is a function of distribution system demand. During daytime hours the reservoir is supplying water for normal and peak demands but during low flow conditions in the early morning hours the system may be designed to fill the reservoir, thereby causing at least a once-daily flow reversal.

It is also common practice to chlorinate the outflow of a surface reservoir. This in itself is not an easy task. However, to provide adequate and reliable chlorination for a reverse flow condition is even more challenging.

The usual method of chlorination control solely by flow pacing from a primary meter is a risky practice because of abnormally wide daily flow ranges experienced by these reservoir systems. Systems designed for flow reversal have much wider flow ranges because the flow has to reach zero before it can reverse. Therefore in every one of these systems the range is infinite, i.e., zero to any maximum value.

Chlorination control for reservoirs will be discussed below in two categories: (1) outflow only and (2) unpredictable reversal of flow. However, it is necessary first to discuss primary meters and reverse flow detection.

*Primary Flowmeters.* There is a wide variety of flowmeters available, but none have the accuracy to provide the necessary chlorine dosage control over the flow ranges experienced at the majority of these systems. The designer or operator should accept the flow meter as most accurate and acceptable for chlorinator control in the range of 4:1. Therefore these chlorination systems should be supplemented with residual control. Retrofitting existing systems using existing flow meters must add residual control. The principal flowmeter accessory for chlorination control is an analog flow signal transmitter, preferably 4–20 mA or 10–50 mA. A pneumatic signal is acceptable but not preferred for a variety of reasons. The reasoning behind establishing an "accurate" range (4:1) for the flowmeter is to allow this signal to blend properly with the residual signal. This is described below.

*Flow-Reversal Detection.* This is a difficult task in any hydraulic system because the basic requirement is the ability and assurance of being able to detect zero flow. Reliable devices such as the thermal probe system[30] are expensive. Laminar-type flow switches that flex with the water flow are inherently insensitive to flows less than about 0.5 ft/sec. Other devices that operate on a turbine-type movement are more sensitive

The need for a flow reversal switching device in a chlorination system is a site condition requirement. The user may find it desirable to shut the chlorination system down during this period, or be able to actuate valves to direct reverse flow to a compartmented reservoir.

Any chlorination system dealing with a reverse flow condition must have added protection of adjustable time delay relays. These relays will protect the chlorination control system from chatter due to the oscillating prism of water usually encountered when the flow makes the transition from forward to reverse. Appropriate switch gear can lock in the forward or reverse function long enough to allow the system to stabilize in either direction.

*Reversal Detection by Chlorine Residual Analyzers.* This type of reservoir chlorination system requires two chlorine residual analyzers arranged as shown in Fig. 9-58. In order to explain the operation of the analyzer control system the function of each principle element of the system will be described.

1 *Chlorine diffuser.* This is the jet injection type for a pressurized conduit. For pipes 36 inches in diameter or less, terminate the nozzle $D/6$ inches from inside wall. For conduits larger than 36 inches, use an across-the-pipe diffuser perforated across the middle third of the diameter (see Fig. 9-40a). The injection nozzle should be fitted with an orifice to provide an exit velocity of 22–26 ft/sec. Use the same velocity for the across-the-pipe diffuser. This diffuser design will eliminate the need for a mechanical mixer provided that the sampling taps are approximately 10 diameters from the chlorine diffuser.

2. *Injector water supply.* Design piping and injector pump to provide as much water as the injector will allow regardless of chlorine flow rate. This will enhance mixing and help to maintain a reasonably constant loop time over a wide water flow range.

3. *Injector location.* The injector should be placed as close to the point of application as is practical.

4. *Sample taps.* The sample taps for each of the analyzers should terminate at the center of the pipe for diameters up to and including 36 inches. For larger pipes the sampling taps should be made the same as the chlorine diffusers. The sample piping for Analyzer No. 2 should be designed for about 3 gpm at 5 ft/sec to provide a scouring velocity and to minimize loop time. Diffuser-type taps should have sufficient holes to limit the entrance loss to 1 ft.

5. *Injector water pump.* This pump serves three functions: (1) it operates the injector; (2) it provides excess injector water to insure good mixing and a more constant loop time; (3) it provides sample water to both analyzers.

6. *Analyzer No. 1.* This analyzer controls the chlorine residual in the outflow water to the distribution system. It is assumed there will always be a chlorine residual in the sample line to this analyzer.

7 *Analyzer No. 2.* This analyzer operates on the biased sample principle. This arrangement is necessary in order that the analyzer may stay in calibration, i.e.,

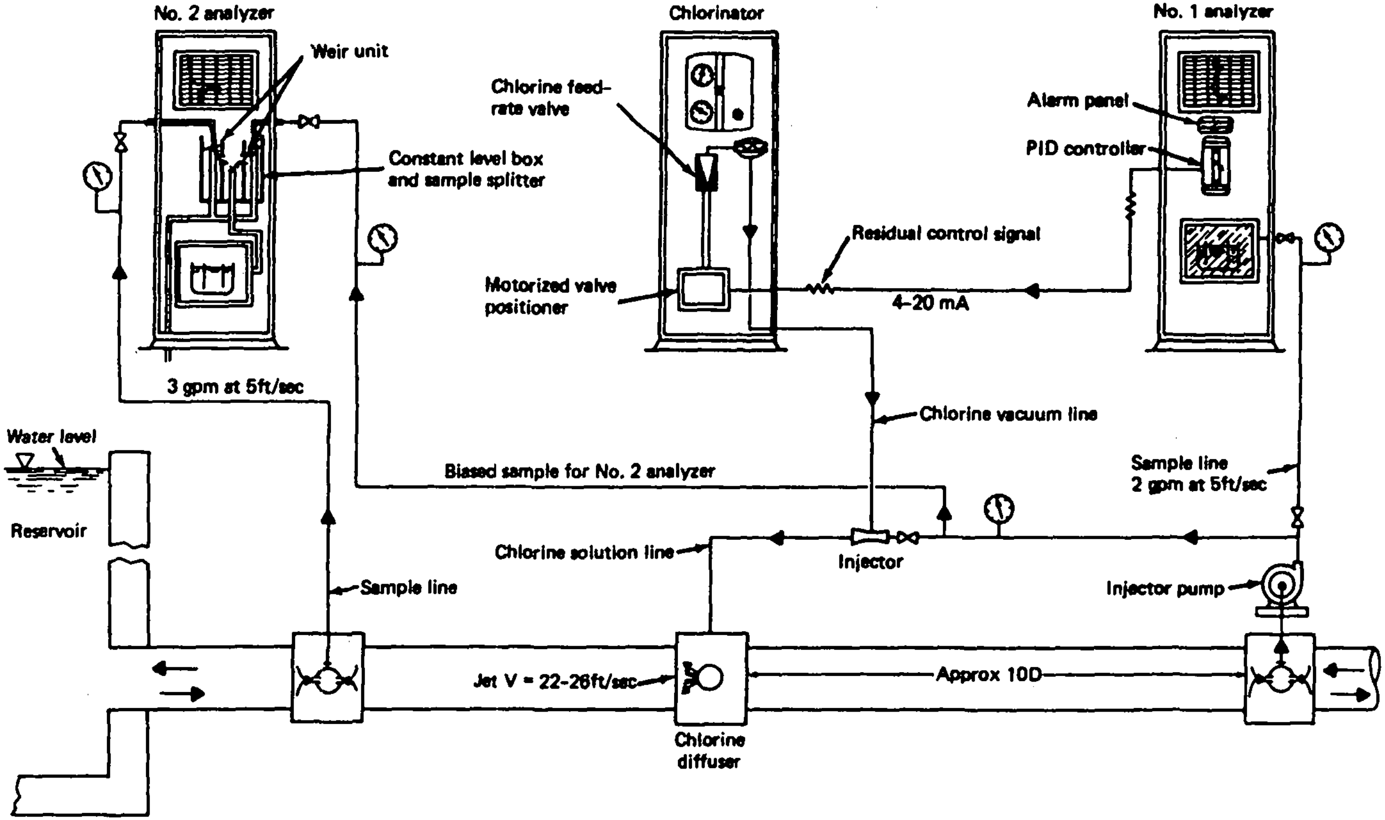

Fig. 9-58. Flow reversal detection and direct residual control using two residual analyzers (unpredictable reversal).

it must not be exposed to zero chlorine residual for any length of time. This is the analyzer which detects the flow reversal, as described below

This system controls the chlorinator feed rate in the outflow mode by direct residual control, as described in "Control Strategies," earlier in this chapter. Assume the residual control band is set between 0.4 and 0.6 mg/l. In the forward direction both analyzers will be receiving a sample in this band range, except that Analyzer No. 2 cell will receive a sample diluted 1 : 1 with unchlorinated reservoir water. Therefore this analyzer will actually be "seeing" a residual in the 0.2–0.3 range. This is sufficient to maintain its calibration equivalent to Analyzer No. 1.

When the reservoir flow begins to reverse to the inflow mode nothing much will happen for several minutes. Then there will be evidence of residual decay in the distribution system and Analyzer No. 1 will call for more chlorine; this will not be seen by Analyzer No. 1 but will appear as a residual increase on Analyzer No. 2. When this residual (which is diluted) reaches an arbitrary level—say 0.6 mg/l on Analyzer No. 2—an adjustable residual alarm switch is tripped actuating a time delay relay which "freezes" the chlorine feed rate at that dosage level and locks out the residual control signal from Analyzer No. 1.

When the reversal begins to change to the outflow mode the chlorinated portion of the reservoir inflow water will pass by Analyzer No. 2 without incident and begins to register on Analyzer No. 1. By field observation of this occurrence the operator will be able to determine where to set the low-residual alarm switch on Anlyzer No. 2. This probably will be about 0.1 mg/l. When this low-level alarm switch is tripped it actuates a time delay relay which restores the automatic chlorinator controls to analyzer No. 1. The key to success of this system or any direct residual control system is a short loop time, 60–75 sec at average flow, and good mixing by short circuiting the chlorine solution to the sample tap by utilizing the injector water pump as a sample pump.

### Water Treatment Plants:

*General Discussion.* A chlorination station for a conventional treatment plant should be designed for precise control, flexibility, reliability, and safety. It should also be provided with the necessary monitoring equipment and alarms for critical functions plus the required safety equipment for dealing with chlorine emissions. The principle considerations are: points of application, chlorinator capacity, control system, contact time, monitoring and control analyzers, injector system and chlorine solution lines, safety equipment, and standby equipment.

*Points of Application.* This is the first consideration because it prefaces the number of chlorinators required. In spite of the recent concern about the THM formation resulting from prechlorination this remains one of the crucial points of application. This is described in Chapter 6. Normally this point is located to allow 2 or 3 minutes contact time ahead of the flash mixers. Although the plant may be designed to use the free residual process and carry a free residual through the entire plant to the clear well, an intermediate point of application should be provided just ahead of the filters. This point may be used intermittently on a manual basis for shock-type treatment to clean up any filter biofouling that may occur.

The other point of chlorination would be for final disinfection or postchlorination for distribution system residuals. In some plants that use the free residual process, this point of application is used for dechlorination to trim the residual entering the distribution system.

*Chlorinator Capacity.* Somewhere in the plant there will be a flowmeter with a given range. The range of this meter should be the basis for the chlorinator capacity. For example, the engineers may be talking about a 10 mgd plant but will be providing a 20 mgd flowmeter. To simplify chlorinator selection, provide a pre- and postchlorinator with the capacity to treat 20 mgd—the full range of the flowmeter. Then if one or the other is not in continuous use it can be used for pre- and/or intermediate chlorination or as a standby. In any event, one chlorinator must be available for standby service.

The actual capacity of the equipment must be calculated on the basis of the 30 min chlorine demand of the water to be treated. Chapter 6 delineates chlorine dosages for the various points of application.

*Control System.* If prechlorination is to be continuous it should be flow-paced controlled and monitored by a residual analyzer after a 15–20 minute contact time. Prefilter chlorination should be manually controlled only. Postchlorination should be under a combination of flow-paced and residual control. Flow pacing for prechlorination should be from an influent meter and postchlorination from an effluent meter. Flow pacing prechlorination by an effluent meter or postchlorination by an influent meter should never be attempted. The time lag and intermediate uses of plant water for backwashing, etc., destroys the control function of flow pacing.

*Mixing.** If the chlorine diffusers are designed in accordance with the recommendations of the "Diffuser Design" section of this chapter, there will be no need for additional mechanical mixers. See Fig. 9-40a.

*Contact Time.* The only contact time that may be critical in a conventional treatment plant is postchlorination. Usually the clearwell is used as a contact chamber. Otherwise the transmission line may be used to provide the necessary contact time before the water reaches the first consumer.

If the treatment plant is relying upon a free residual for disinfection, 10 minutes contact time is sufficient. If chloramine treatment is used the contact time should be increased to 50–60 minutes.

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* See also diffusers as a mixing device in Chapter 8.

*Monitoring and Control Analyzers.* Chlorine residual analyzers should be used to monitor all prechlorination activities. Also analyzers should be used to monitor and control the residual in the water entering the distribution system. Large water systems will also find it useful to monitor chlorine residuals at strategic points or trouble spots in the distribution system.

*Safety Equipment.* All treatment plant chlorination stations should be equipped with the safety equipment described under that section.

*Injector System and Chlorine Solution Lines.* Experience has demonstrated it is preferable to locate the injectors adjacent or near to the diffusers. The use of remote injectors eliminates the temptation to manifold the chlorine solution lines in the chlorinator room. Manifolding solution lines and using rotameters to split the chlorine flow downstream from the injector is excessively costly and reduces the chlorination system to an uncontrollable hazard resulting in an operator's nightmare. Locating the diffuser adjacent to the point of application requires that there be no more than one diffuser per injector and no more than one injector per diffuser. In some cases the vacuum lines to the various injectors may be manifolded at the chlorinators to achieve redundancy—but splitting the chlorine solution discharge from the injector should not be permitted.

## CHLORINE RESIDUAL ANALYZERS

**Historical Background.** There are two methods by which the chlorine residual can be continuously analyzed: colorimetric and amperometric.

The colorimetric method, using orthotolidine reagent, has been tried and discarded many times. Wallace and Tiernan Company began investigating the possibilities of automatic chlorine residual control using orthotolidine about 1927. Units were developed that could continuously record the O-T residual and at the same time adjust the chlorinator feed rate. The first of these was installed in 1929 at Little Falls, NJ; the second, in 1930 at Rahway, NJ.[31] A modification of these units was installed about 1930 in Los Angeles,[32] and operated for many years. One of these units is shown in Fig. 9-59. The latter units differed in that the O-T residual analyzer had a fixed color disk for a given O-T residual of 0.3 ppm. If the color in the analyzer did not match that of the disk, the error signal between the two drove the control valve on the "trimming chlorinator" until the two colors matched and the error signal became zero. The residual record then was one of deviation. Some years later Caldwell[33] developed an O-T recorder based on Harrington's work,[34] using neutral orthotolidine. The colorimetric recorders fell into disuse primarily because the photoelectric cells were not able to differentiate accurately enough between the relatively small changes in the color representing a residual change. Also, after it was realized how important free chlorine residual was, compared to total chlorine, another method had to be found, since it was not practically

Fig. 9-59. Colorimetric O-T analyzer used for chlorine residual control by City of Los Angeles Dept. of Water and Power from 1930 to 1950s at McClay Highline Station.

possible to do this with orthotolidine.[35] In addition, awkward mechanical operation helped make the system impractical.

Circa 1955 Fischer and Porter Co. developed a sophisticated O-T analyzer which survived for a few years until their amperometric analyzer was developed. Hach Chemical Co. also marketed an O-T analyzer about this same time which was unable to survive competition from the amperometric analyzers. However, Hach did introduce the first successful DPD colorimetric analyzer in 1980. This unit is described below.

The search for a better method of chlorine residual determination resulted in the development by H. C. Marks of Wallace and Tiernan Company, about 1942,[36] of the amperometric titrator, in part inspired by Griffin's work in 1939–1940 on the breakpoint phenomenon. The first amperometric chlorine residual recorder was placed on the market by Wallace and Tiernan Company about 1948. Among the first installations were those at Wyandotte, MI,[37] Allentown, PA,[38] and Brantford, Ontario, Canada. Results from these early installations proved so dramatic that continuous residual recording became popular in the treatment of public water supplies. Operating experience from these installations demonstrated two important characteristics of the amperometric cell. These were predictable changes in cell output current due to changes in sample temperature and *p*H. Changes in *p*H were corrected by additions of *p*H 4 buffer solution, and temperature was corrected by either manual adjustment or automatically by the installation of a thermistor.[39] Most current models come equipped with a thermistor.

During this period Wallace and Tiernan company made a polarographic cell for the City of Chicago Water Department which was arranged to measure combined (chloramine) chlorine only. It did not require chemicals but it used a large sample, 1 liter per minute. Twenty years later, when Chicago built the Central Water Filtration plant, analyzers were required to measure free chlorine only. The same type of analyzer was used except that the applied voltage across the electrodes was changed. This made the same cell specific for free chlorine.

Since the 1970s two notable contributions were made. The first was the development by Morrow[40] for Fischer and Porter Co. of the Chlor-Trol analyzer, which was capable of measuring free chlorine in a sample containing significant chloramine concentrations. The second was the development of the selective membrane electrode by Johnson et al.[41] By this time many companies were actively engaged in developing instrumentation for continuous chlorine residual measurement. These participants included Foxboro, Orion, Uniloc (Rosemount), Delta Scientific, Enterra, Chlortect, and IBM. Other accomplishments have been modifications that have extended the use of chlorine residual monitoring in wastewater, and finally the step from monitoring to automatic residual control.

The step from residual recording to residual control took nearly ten years to gain acceptance in the United States. Residual control was being used in England for the London water supply as early as 1950 and for controlling superchlorination and dechlorination stations of underground supplies where the only other treatment was microstraining.

The use of continuous residual analyzers for wastewater chlorination began circa 1960. The immediate purpose was to control the chlorination system. Prior to 1960 there was limited use of analyzers on highly polished tertiary effluents. The pathway to successful analyzer operation on wastewater effluents has been a rough one. One of the first successful installations on secondary treated effluents was made at the Napa Sanitary District, Napa, CA in 1961, where the unit installed was the same as the version used for potable water, except that a motorized filter was installed on the analyzer cell sample line.

When this unit was tried for operation on primary treated effluent, various problems were encountered which were related to the quality and characteristics of the wastewater. The high grease content in the primary effluent is particularly bothersome in that it coats the electrodes. The insulation effect of the grease causes a severe distortion of the calibration, resulting in erroneous readings. This became an unwarranted maintenance problem.

The amount of buffer solution required to lower the $pH$ of most primary effluents is very high, and an appreciable excess of iodide is also necessary to make the reaction with combined residual chlorine proceed as fast as possible. This made the chemical cost of operation a most significant factor.

Experience has shown that chlorine residual analyzers are not reliable for use with primary effluents owing to the poor quality of the sample, and the inability to maintain a sample flow through the cell. Another factor discouraging to operating personnel is the time required to keep the electrode surfaces clean enough to maintain system calibration. Recalibrations for primary effluent samples need to be made at least twice a day.

For many years chlorine residual control was used solely as an adjunct to flow-paced control. Now there are many installations controlled solely by chlorine residual.

The advent of the programmable controller has stimulated interest in the use of residual control. This type of instrumentation allows the precise formulation of a residual control system to any site-specific case.

## General Discussion and Definitions:

*Amperometric.* Continuous analyzers which use two electrodes for measurement are usually categorized as *amperometric.* This was true when referring to the original Fischer and Porter and Wallace and Tiernan analyzers. However, it is no longer true with the array of analyzers currently available.

Electrode reactions are characterized by the transfer of electrons between the electrode and substances in the sample solution. The electrode reaction which initiates the electron transfer results in the flow of current between the electrodes. When the electrode reactions occur spontaneously upon short-circuiting the two electrodes, the system is described as a *galvanic cell.* If, however, the reactions are forced to occur by the imposition of an external electromotive force the cell is referred to as an *electrolysis cell,* i.e., the generation of chlorine. In the above definitions the term "reactions" refers to the chemical changes of the solution which might occur. In the measurement of chlorine residuals the current flows between the electrodes primarily as a characteristic of the species involved. The dual electrode analyzers like those made by Capital Controls, Fischer and Porter, and Wallace and Tiernan are galvanic cells—amperometric type. These cells respond in a linear fashion only to the elemental halogens, i.e., bromine, chlorine, and iodine. They do respond to most chloramines, but not in a linear fashion.

*Voltammetry.* When the galvanic cell is subjected to an external applied voltage to provide the measurement of a particular chemical species in the presence of other species the system is described as *voltammetry.* In this case the voltage applied provides qualitative information on the electroactive substance present and the current measured provides the quantitative information of the species selected by the applied voltage. This technique is used to isolate the free chlorine species that ocurs in the presence of chloramines. This is a variation of the *amperometric* measurement technique. The use of the term *amperometric* has come into use to indicate concentration measurement based upon the measurement of the current flowing between two electrodes at a constant potential at the indicator electrode.

*Polarography.* This is a broader term used to describe analytical measurement of trace materials in solution, metallic ions, etc.[42] This method utilizes the principles of voltammetry, i.e., current–voltage curves, but with a polarographic cell. A polarographic cell is an electrolytic cell consisting of a nonpolarizable reference electrode, a readily polarizable electrode, and an electrolyte solution containing electro-oxidizable or electro-reducible material.

At this point the difference between a polarized and a depolarized electrode should be understood. An electrode is said to be polarized when it adopts the externally impressed potential (voltage) on it with little or no change in the rate of the electrode reaction, i.e., no change in current. Therefore if only one electrode in the cell is polarized, its potential changes in the same amount as the change in applied voltage.

At the other extreme an ideally depolarized electrode is one that retains a constant potential regardless of the magnitude of the current flowing between the electrodes. Therefore the nonpolarizable electrode potential is not altered by the changes in the externally applied voltage.

When an increasing electromotive force (applied voltage) is impressed across the electrodes of a polarographic cell, and if the resulting current is plotted as a function of the applied voltage, a curve is obtained as shown in Fig. 9-60. The extension of the wave curve along the current axis is directly related to the concentration of the material in the solution sample and its inflection point (0.8 V) is at the applied voltage which is characteristic for this particular species of material. Examples of this type of cell for measuring species of chlorine residual are described below.

*Potentiometry.* This method is used for measuring trace materials in solution by means of an electrode containing two sensing elements. The method is based upon the constant current technique of species separation which measures the potential at each element. It is not widely used in the measurement of chlorine residuals.

The potentiometric method for chlorine residual is only applicable to the measurement of total residual chlorine because it measures the iodine species released from the potassium iodide electrolyte oxidized by total residual chlorine. A platinum (redox) sensing element develops a potential which depends upon the relative concentration of the iodide and iodine species in the sample. The second element,

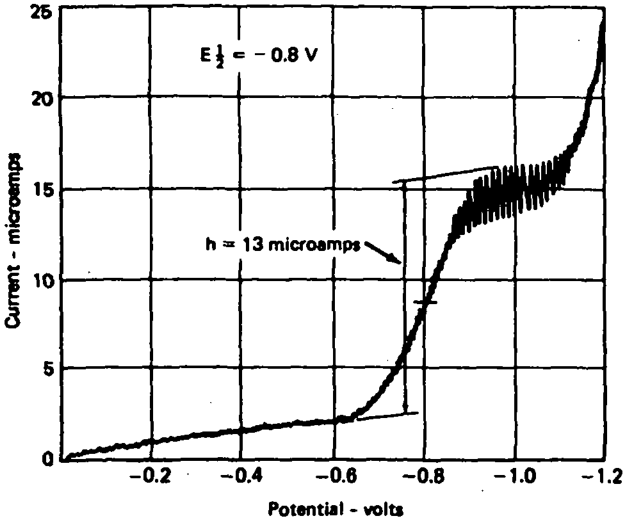


Fig. 9-60. Polarographic curve.

the iodide element, develops a potential that depends upon the iodide ion concentration in the sample. The electrode then in turn measures the difference between these two potentials developed at the two sensing elements. The net potential represents the iodine concentration directly related to the total residual chlorine as measured in the amperometric method.

**Designer's Evaluation Check List.** The following limitations should be examined when selecting or evaluating an analyzer for site-specific conditions.

*Species Measurement.* The most important function of any analyzer is its ability to measure any given species of chlorine residual without interference from other species present in the sample. For example, how dependable can a given analyzer be for measuring free chlorine residual in the presence of some chloramine residual? What proportion of chloramine residual will interfere with the accuracy of the free residual measurement? This is part of analyzer accuracy limitation.

*Accuracy.* This is the agreement between the amount of a component measured by the analytical method and the amount actually present. It is usually expressed as percent of full scale over a specified range.

*Precision.* This is referred to as reproducibility of measurement when repeated on a homogeneous sample under controlled conditions. Normally this should be expressed in percent of the full scale reading over a specified range.

*Sensitivity.* This is described as the least concentration of chlorine species detectable in any given sample.

*Range.* This is most important. Some analyzers are limited to a detectable range of only 0–2.0 mg/l. Analyzers capable of 0–10 or 0–20 mg/l are preferable to those with a limited range.

*Response Time.* This characteristic is of prime importance if the analyzer is to be used for residual control. The manufacturer usually expresses this time as that necessary to provide a percentage response to a step change in residual concentration after the sample has entered the analyzer.

For residual control purposes the 90 percent response time should not exceed 10 seconds and initial response should occur in less than 10 seconds.

*Temperature Compensation.* All analyzers should be equipped with thermistors to compensate for temperature variations in the sample. These variations affect the response time and current output of the electrodes. Colorimetric analyzers experience major changes in response time due to changes in both sample and ambient temperatures.

### Wallace and Tiernan, Division of Pennwalt Corp.:

*General Discussion.* This family of continuous analyzers was the first to be marketed for measuring chlorine residuals. These analyzers can be divided into three categories: potable water, wastewater, and cooling water. The first two are amperometric. The third type (cooling water) is polarographic. They are described below.

*Amperometric Cell. Theory of Operation.* Fig. 9-61 illustrates a typical arrangement of the analyzer cell. The measuring electrode is copper and the reference electrode is either platinum or gold. The electrodes are mounted coaxially so that the sample water flows continuously through the cell. The cell produces a small (0–150 microamp) DC current proportional to the amount of free halogen (chlorine, bromine, iodine, chlorine dioxide) in the sample. However, since the cell is capable of measuring an oxidation reaction the cell will also produce a current due to the presence of chloramines in the sample. This response is not linear, but acts to interfere with free residual measurements. The limiting range of these cells is 0–20 mg/l, but they are available in ranges of: 0–1, 0–2, 0–5, 0–10, and 0–20 mg/l. The current response is linear over the entire range of 0–20 mg/l. Speed of response is 10 seconds or less.

The basic principle of this cell is that a current will flow between the two electrodes proportional to the free halogen concentration in the flowing sample. To measure this current the electrodes are short circuited.

A minor flow of current will always be present even in the absence of a free

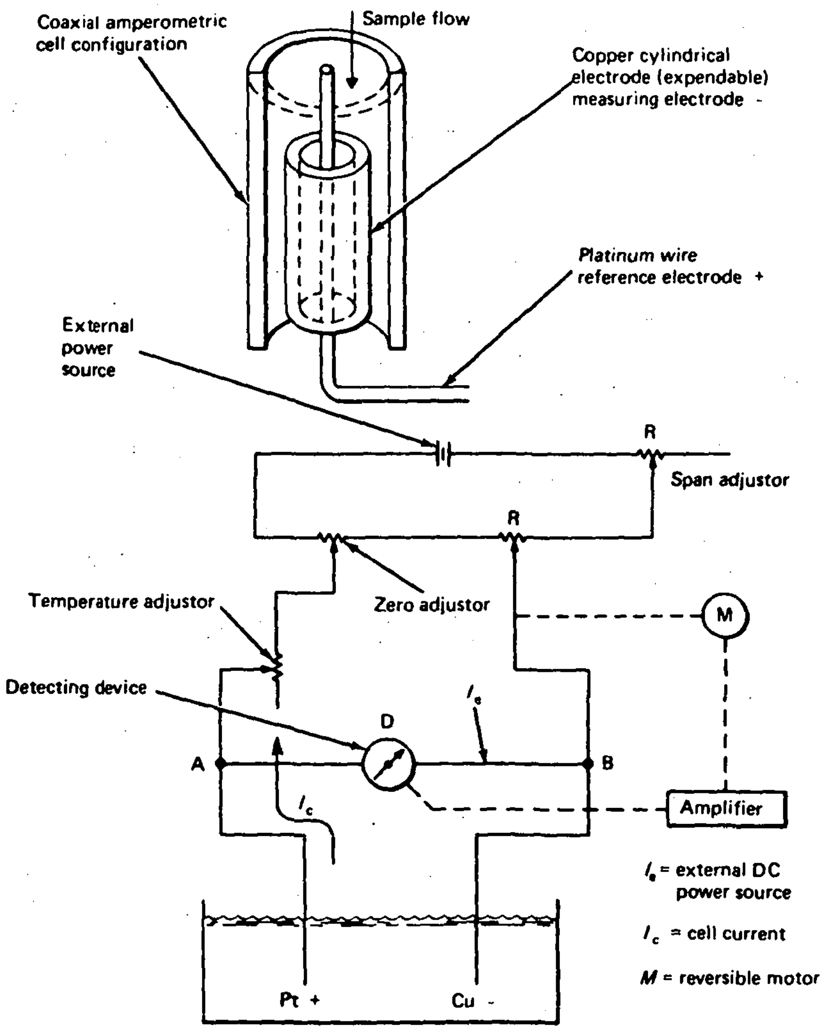


Fig. 9-61. Details of amperometric cell for chlorine residual analyzer (courtesy Wallace and Tiernan Division, Pennwalt Corp.).

halogen; therefore the current detecting device must be able to delete this current. This is shown as the zero adjustment in Fig. 9-61.

There are two ways of measuring the current produced by an amperometric cell. One way, illustrated above, measures the current flow directly. The other way is to pass the current through a known resistance and measure the potential drop. This is known as the IR drop method (see "Capital Controls").

Referring to Fig. 9-61, an external DC power source is used for comparing

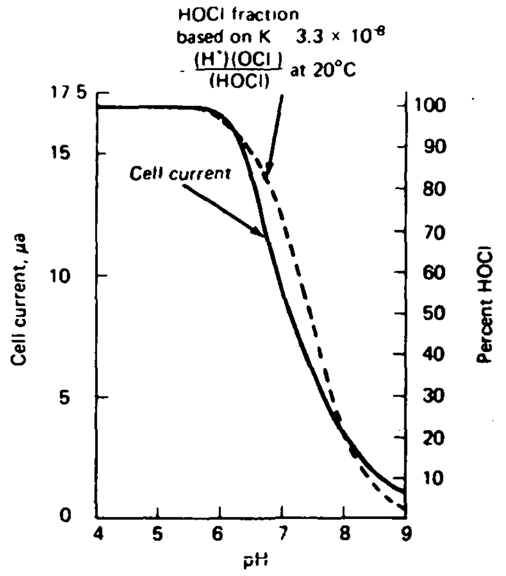


Fig. 9-62. Effect of pH on amperometric cell current. (All values are for 1.0 mg/l free chlorine residual.)

the current produced by the free halogen concentration in the cell. Current flows from *A* to *B*. As this current increases, the detecting device *D* indicates this and generates a signal which is amplified and drives a reversible motor which positions a slider *R*. This movement increases the current from the external power source, which flows from *B* to *A*. As soon as the increase from the external source is sufficient to balance the potential between *A* and *B*, the motor stops and the recording or indicating mechanism comes to rest (null position) at the new value of an increased current generated by the free halogen in the amperometric cell.

*p*H *Effect*. Current flow in amperometric cells are grossly affected by changes in *p*H. Fig. 9-62 illustrates the magnitude of this effect upon a 1.0 mg/l free chlorine residual. This is called the *p*H coefficient. It is dealt with in either one of two ways by Wallace and Tiernan analyzers: addition of either carbon dioxide gas, or liquid sodium acetate—acetic acid (*p*H 4 buffer) to the sample.[43] The cell current is most stable in the *p*H range of 4 to 4.5. The amount of buffer required depends upon the alkalinity of the sample. The analyzer is designed to meter either type of buffer additive.

*Temperature Effect*. All amperometric cells respond to changes in sample temperature. The change in cell current due to temperature change in the sample for a fixed residual is mathematically predictable, and therefore can be automatically compensated by the installation of a thermistor[39] in the circuitry as shown (temperature adjuster).

*Diffusion Phenomenon.* This condition was first recognized by Marks and Campbell in 1950.[44] When the cell current approaches zero or remains at zero in the absence of free halogen residual, a concentration of electrons begin to accumulate at the measuring electrode, thereby repelling the negative ions. This impedes the speed at which the free halogen can diffuse through the layers of electrons that accumulate under these conditions. Therefore, sample flushing action and electrode bombardement tend to alleviate this condition.

*Electrode Fouling.* The effect of this condition was discovered early in the development of these analyzers. To prevent the sample cell from being fouled by biological slime, organic debris, or chemical deposition (alum floc, ferri-floc) provision is made to continuously recirculate a quantity of abrasive grit which bombards both electrodes and the adjacent cell area. This keeps the electrodes clean and maintains the electrode surface at optimum molecular equilibrium.

*Sample Flow Rate.* Current flow in the cell will vary with sample flow rate. It must be observed that in calibrating an analyzer with a sample containing free halogen, the zero check and adjustment is made by stopping the sample flow. This demonstrates the effect of sample flow rate upon cell current. The sample hydraulics must be such that the flow through the cell will be constant. Variable pressures in the sample source must be controlled by a suitable external pressure regulating valve.

*Zero Current Effect.* It has been observed that there is no practical means of calibrating the amperometric cell when free halogen is absent from the sample. Consider the zero check described above, i.e., completing the zero adjustment with the sample flow stopped while the sample contains a significant concentration of free halogen. When a sample not containing any free halogen is passed through the cell the analyzer will always indicate a slightly negative reading—below zero.

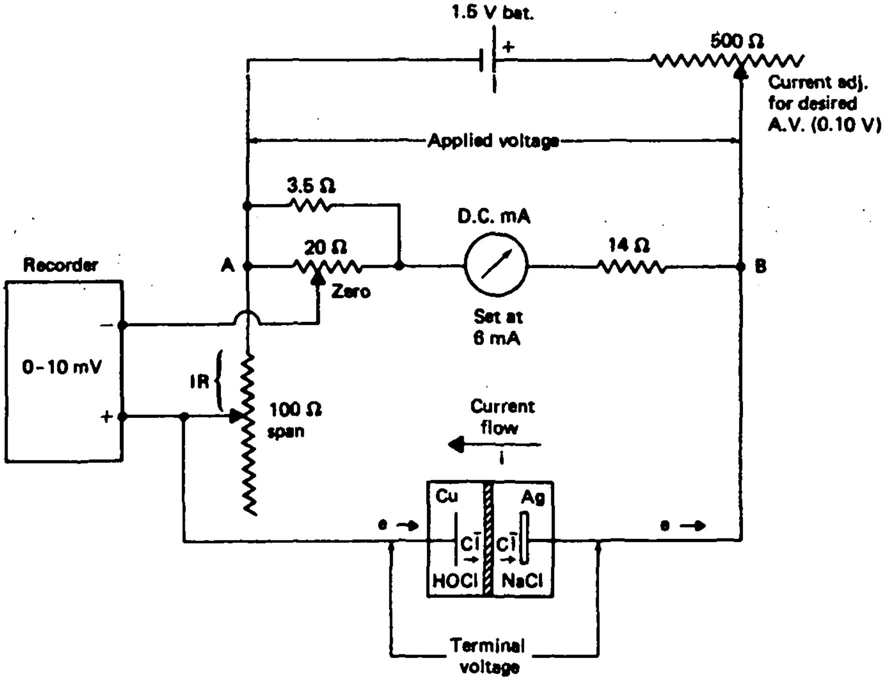
*Potable Water Practice.* The analyzer for this purpose is described in Catalog No. 50.245. It can measure either free or combined chlorine. This analyzer has been successful in monitoring and controlling the free chlorine residual process for many years. The operating experience that has been accumulated indicates clearly that the treated water total chlorine residual should contain at least 85 percent free chlorine. When this analyzer is arranged to control or monitor free residual in the presence of combined residual, interference from the combined chlorine will be about 10 percent of the total residual chlorine at sample *p*H 4.5.[45]

When total residual chlorine is to be measured (free and combined) it is necessary to add potassium iodide along with the buffer solution. Total residual chlorine in the sample at *p*H 4.0–4.5 will release free iodine in proportion to the total chlorine residual. Therefore the amperometric cell will generate a current in proportion to the free iodine liberated from the potassium iodide.

The Wallace and Tiernan cell requires a sample flow of 360 ml/min. At this rate 15 g KI/l/mg/l total chlorine residual is required. Normally the KI comes in tablet form at 3 g/tablet. The tablets are dissolved into the buffer solution.

*Wastewater Practice.* The analyzer for wastwater is considerably different from the potable water model. It is described in Wallace and Tiernan Catalog No. 50.215. This unit is a modification of the potable water unit. It is designed to process low quality wastewater effluent. A sample dilution system (with fresh water) is provided to reduce chemical cost (*p*H 4 buffer and KI). A motorized filter is installed in the incoming sample line to eliminate the sample debris encountered in treated sewage. This analyzer requires the same amount of KI per mg/l of total chlorine. Allowance must be made for dilution water added.

*Polarographic Cell.* This cell uses a reference electrode and a measuring electrode illustrated in Fig. 9-63 and is described in Wallace and Tiernan Catalog No. 50.236.



Electron is from Cu Ag (opposite to current flow)
Terminal voltage = A.V. − IR drop across span potentiometer
Applied voltage = Total IR drop across AB
Applied voltage = 0.006 X (14Ω + 3Ω) = 0.102 V approx.

Fig. 9-63 Polarographic cell (courtesy Wallace and Tiernan Div. Pennwalt Corp.).

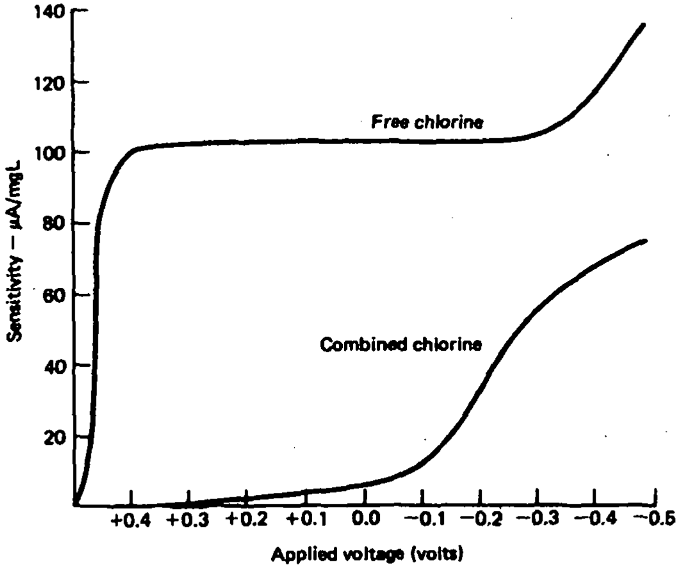


Fig. 9-64. Polarographic curve showing free chlorine versus chloramines.[58]

The measuring electrode is the only electrode that is in the sample. This cell is capable of measuring either free chlorine or free iodine and it does not require any $p$H buffering or potassium iodide. The use of applied voltage to the electrodes allows the selection of either chlorine residual species. Fig. 9-64 demonstrates that the free chlorine voltage current measurement curve obtains at +0.3 V applied voltage while combined chlorine obtains at −0.07 V (approx.). In this cell the reference electrode is silver–silver chloride and the measuring electrode is platinum. The range of this analyzer is limited to 0–2 mg/l free chlorine. It is not affected by $p$H changes in the range of 5–8.5, nor is it affected by the presence of combined chlorine residual. Since no chemicals are added to reduce $p$H, a true sample is analyzed. Changes in salinity and the presence of such cooling water treatment compounds as chromates, phosphates, and defoamers do not interfere with its accuracy. A thermistor compensates for sample temperature changes between 35°F and 120°F. Grit is replaced once a month and electrolyte tablets (NaCl), once every 3 months. This unit was designed specifically for condenser cooling water systems.

## Capital Controls:

*General Discussion.* Two amperometric analyzers are offered. The flow diagram is shown in Fig. 9-65.[46]

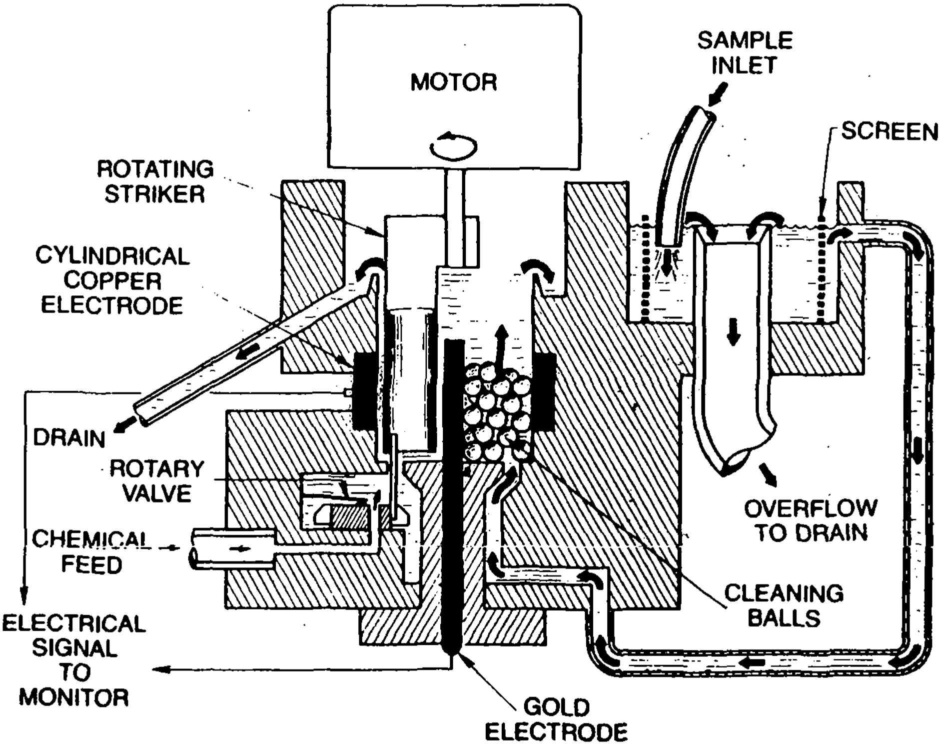


Fig. 9-65. Amperometric analyzer flow diagram (courtesy Capital Controls Co.).

No. 871. This is for the measurement of free chlorine. Analyzer includes a single reagent feed system for feeding *p*H buffer solution.

No. 872. This unit measures total residual chlorine. It is furnished with two separate reagent feed systems. One for *p*H 4 buffer solution and the other for potassium iodide solution.

Both the buffer solution and potassium iodide solution are stored in separate containers (7 days capacity) and fed from constant head reservoirs. Each solution is fed through a rotary valve located on either side of the sensing cell. These valves are actuated by an extension of the striker used to clean the sensing cell. The valves move with each contact of the striker. This provides a precise amount of solution to be fed during each valve revolution.

The sample flow to the filtering chamber should be about 500 ml/min, but only 100 ml/min passes over the overflow weir in the filtering chamber to the cell. This is the amount of sample that needs to be treated with reagents. This sample flow rate is controlled by fixed differential weir levels between the inlet chamber and the cell chamber

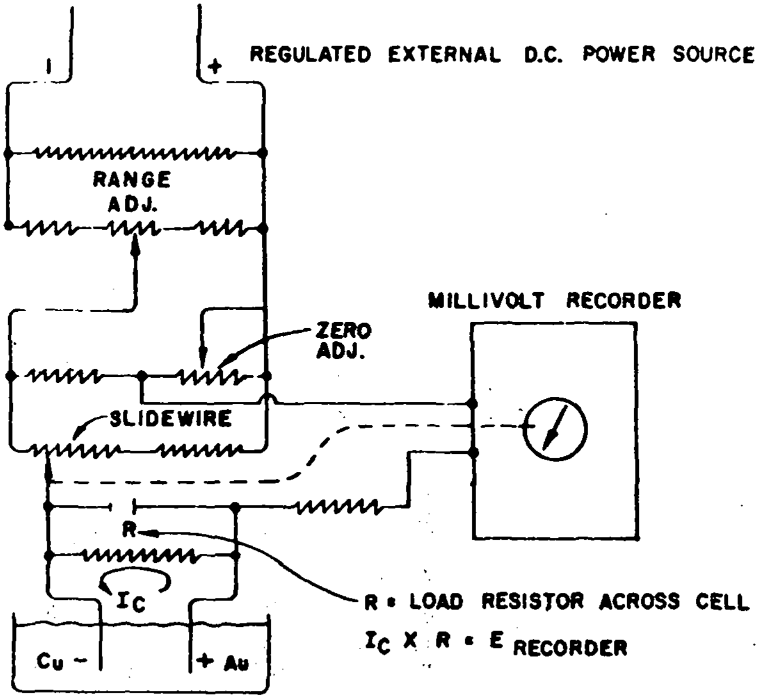


Fig. 9-66. Amperometric cell current measurement by the IR drop circuit.

The surfaces of both electrodes are kept clean by the continuous action of PVC balls agitated by a motor driven rotating striker.

*Residual Measurement.* The cell circuitry for these analyzers differs somewhat from the previously described Wallace and Tiernan analyzers. The cell current is measured indirectly. Fig. 9-66 illustrates a typical *IR* drop circuit which is used in the Capital Control analyzers. The cell current passes through a resistance and the voltage (potential) drop across this resistance is measured. The major difference between this method and the current measurement method is that the external power source is used solely for zero adjustment. This is a necessary feature, since some current will flow in all waters even if a free halogen residual is zero, therefore this natural current must be neutralized.

*The current output* of these analyzers is 50 millivolts at full scale. These units are offered in ranges of 0–0.5, 0–1.0, 0–2.0, 0–3.0, 0–5.0, 0–10, and 0–20 mg/l.

*Sensitivity* is 0.01 mg/l.

*Speed of Response.* About 4 seconds elapses from the time the sample enters the analyzer to the first signal indication of changed residual. Full-scale residual change requires 1.5–2.0 minutes to reach correct indication—depending upon analyzer range.[46]

### Delta Scientific (Xertex):

*Historical Background.* The 1984 models marketed under the above name derives from the research and development work by Johnson, Edwards, and Keeslar.[47,48] The importance of developing an instrument to measure undissociated HOCl was reported by White[49] in 1974. The purpose of such an instrument was to equate more precisely the germicidal power of free chlorine in terms of residual measurement. All of the existing methods measure HOCl plus $OCl^-$. It is well documented that the germicidal efficiency of the HOCl fraction is 80–100 times that of the $OCl^-$ ion (see Chapter 4). Therefore measurement of HOCl alone instead of $HOCl + OCl^-$ would provide a more realistic relationship between "Free chlorine" and germicidal efficiency.

The Johnson cell was designed as a direct and selective amperometric membrane electrode for the exclusive measurement of undissociated HOCl in the presence of $OCl^-$, combined chlorine, and other interferences found in the control of disinfection by chlorine in natural waters.[48] The sensor was described as a polarographic cell. It consisted of a silver anode immersed in a 1.7 *M* KCl solution and a gold cathode. The gold measuring electrode was separated from the "HOCl porous" membrane. The silver/silver chloride half cell acted as the reference electrode. The membrane is used to establish a diffusion-limiting barrier next to the cathode (gold electrode). Any oxidizable compounds able to diffuse through the membrane are reduced, which generates a flow of current within the cell. Membrane selectivity was further provided by a positive voltage applied to the cathode. This positive voltage makes it difficult for $OCl^-$ and chloramines to be reduced (i.e., obtain electrons). Research by Johnson et al.[48] revealed that interference by $OCl^-$ ion was 0.0 percent, monochloramine 1.3 percent, dichloramine 3.0 percent, and nitrogen trichloride 725 percent. Interference by $NCl_3$ would be disastrous to any attempt to measure free chlorine after breakpoint in some waters.

On the basis of the above research and several years of development, Delta Scientific marketed three models as a division of National Sonics, then a part of Envirotech. The first model was based upon the Johnson cell, designed to "measure disinfecting power"—more specifically, it was intended to measure undissociated HOCl in the presence of $OCl^-$ and chloramines. This was the Series 8224/8324 HOCl analyzer.[50] The second model, Series 8225/8325, was designed to measure all chloramine species and hypochlorous acid. This analyzer was intended for the wastewater market. During this period of marketing Delta Scientific altered their stance significantly because of the wastewater market potential. In 1978 they announced their series 8000 Polarographic Wet Chemistry Analyzers:[51] Model PWC-82125 Module (for measuring Total Residual Chlorine), together with a Model 8224 or 8324 Analyzer Transmitter.

Owing to difficulties with the original idea of measuring only HOCl for free chlorine, the sample conditioning module adds *p*H 5 buffer solution to the sample which converts $HOCl + OCl^-$ to all HOCl, which is measured by the Delta polarographic sensor

*To measure total residual chlorine the sample conditioning module adds acified* potassium iodide solution to the sample, converting all of the chlorine residual to free iodine, which is measured by the Delta Scientific polarographic sensor.

Sometime later Delta Scientific made another change by offering a model which was specific for ammonia chloramine species.[52] This was designated the CAC Model 82125 (combined ammonia chloramines). This model contained an electrolyte solution of potassium iodide. The current response between the reference electrode, the electrolyte, and the chloramines diffusing through the membrane at the measuring electrode was proportional to the concentration of molecular triiodide ion

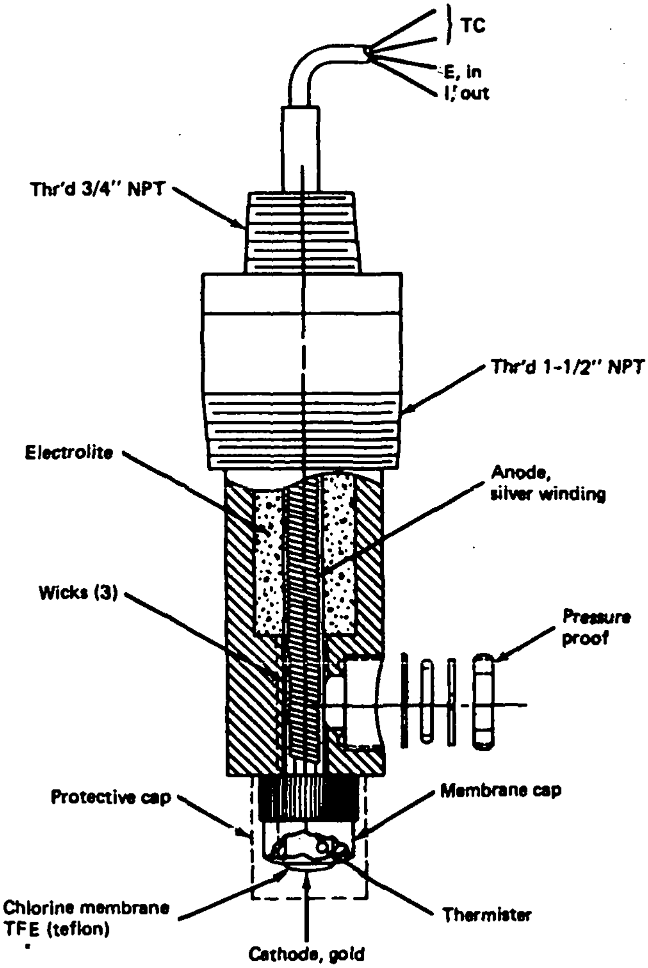


Fig. 9-67. Chlorine sensor polarographic membrane cell (courtesy Delta Analytical Div. Xertex Corp.).

($I_3^-$) produced upon oxidation of iodide by the membrane-permeable ammonia chloramine species. The practical value of this analyzer has never been made clear.

During 1984 Delta Scientific announced a new 900 Series of analyzers. These are digital microprocessor based analyzers which measure sensor current and temperature and sensor output, and accurately compute the chlorine residual species using a polynomial equation. These instruments are described below. To better understand these instrument descriptions the following terminology is used by Delta Scientific: FAC = free available chlorine = undissociated HOCl; TFC = total free chlorine = HOCl + $OCl^-$; TRC = total residual chlorine = HOCl + $OCl^-$ + ammonia chloramine + organochloramines; CAC = combined available chlorine = HOCl + $OCl^-$ + ammonia based chloramines (i.e., mono- and dichloramine).

*Delta Scientific Model No. 924.* This instrument measures either FAC or TFC.[53] Therefore it is specific for free available chlorine and at the same time is subject to interference by both $NCl_3$ and combined chlorine. $NCl_3$ has a gross effect while combined chlorine has a much lesser effect.

If the $p$H is separately measured it can be used to measure either FAC or TFC manually. When it is equipped with a $p$H probe the instrument measures or computes either FAC or TFC, temperature, and $p$H. It provides these results for display and instrument output. Chlorine residual values can be selected for 0–1, 0–5, or 0–10 ppm full scale. The analog outputs for chlorine are 0–10 mV, and temperature is 0–10 mV corresponding to 0–50°C.

This analyzer does not require the addition of any reagents. The heart of this instrument is the chlorine sensor (see Fig. 9–67). This is a classic polarographic cell. It consists of a semipermeable membrane, a silver anode immersed in a salt solution, and a gold cathode. A constant voltage—appropriate for the free chlorine plateau—is applied to the gold cathode. The membrane establishes a diffusion-limiting barrier next to the gold cathode where the free chlorine species, which diffuse through the membrane, are reduced. Residual chlorine diffusing through the membrane reacts electrochemically with the salt solution and causes a current to flow between the gold cathode and the silver/silver chloride reference electrode (anode). The current is directly proportional to the chlorine concentration:

$$I = \left(\frac{nFAP}{b}\right)C = KC \qquad (9\text{-}13)$$

where

$I$ = current, mA
$n$ = number of electrons transferred in the reduction reaction, dimensionless
$F$ = Faraday's constant, mA-sec/mmole
$A$ = area of the electrode, mm$^2$

$P$ = permeability of the membrane to the chemical species diffusing through the membrane, $mm^2/sec$
$b$ = membrane thickness, mm
$C$ = concentration of the chemical species being reduced, $mmole/mm^3$
$K$ = cell constant, $mA\text{-}mm^3/mmole$

The terms $n$, $F$, $A$, and $b$ are constant for any given membrane and chemical species.

The microprocessor operates as follows:

1. It measures the chlorine sensor output and temperature and computes FAC.
2. It measures $pH$ sensor output and computes temperature corrected $pH$.
3. It computes TFC from the temperature-corrected FAC and $pH$, because the concentration of HOCl is also temperature dependent (see Chapter 4).

An internal battery is provided to maintain the polarizing voltage on the gold cathode during power failures. This is a rechargeable battery which is kept charged during normal operation and has a life measured in years.

The speed of response is 90 percent in 20 sec.

Linearity over 0–5 and 0–10 ppm is unknown.

Stability is ±1 percent full scale for 24 hours.

Electrolyte life is approximately 6–9 months.

The electrolyte is 60 ml buffered salt solution.

Detection limit is unknown. Precision is unknown.

This analyzer is designed on the basis of a probe application, i.e., no sample lines required. The sensor can be located up to 50 ft from the analyzer. Sample movement must be not less than 1 ft/sec at the gold cathode.

*Delta Scientific Model No. 925 Chlorine CAC/TRC.*[37] This instrument was designed for wastewater applications and uses a special sensor.[38] The sensor used in this analyzer is physically the same as the Model 924 with the following exceptions: the electrolyte is a buffered potassium iodide solution instead of a salt solution, and the applied voltage to the gold cathode is different. This difference in applied votage allows the sensor to be specific for combined chlorine. This is a typical voltammetric application. Under the above conditions, the analyzer measures CAC, for whatever that is worth.* This mode of measurement does not require the addition of any reagents.

To measure TRC this model analyzer requires the use of the PWC Sample Conditioning Unit. This unit treats the sample with a buffered potassium iodide solution, which converts TRC to free iodine. Delta Scientific advises it is imperative that the $NH_3$–$Cl_2$ ratio to be at least 4 to 1 if the sensor is to work directly in the wastewater stream.[56]

The model 952 analyzer has the same performance characteristics as the model 924.

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[*] Probable widest application would be wastewater effluents.

## Fischer and Porter Co.:

*General Discussion.* Three basic models of analyzers are available for measuring the various chlorine residual species under a variety of conditions. These analyzers incorporate conventional solid two-electrode amperometry. The electrochemical cell consists of a gold (or platinum) measuring electrode and a copper reference electrode. The halogen reaction occurs at the gold cathode. The copper reference electrode is the sacrificial anode. The copper reference electrode is nonpolarizable such that when a potential is applied *across* the two electrodes, the potential at the measuring electrode is the only one that is affected.

*Anachlor™ Series 17B4200C.* This model is used to measure either free or total chlorine.[56] Free chlorine is measured by buffering the sample to $p$H 4 and the addition of potassium bromide. At this $p$H free chlorine will oxidize the bromide ion to free bromine ($Br_2$). The galvanic cell measures the current which represents the concentration of free bromine which is proportional to the free chlorine present:

$$2Br^- + HOCl + H^+ \longrightarrow Br_2^0 + Cl^- + H_2O \qquad (9\text{-}14)$$

and the bromine then reacts at the measuring electrode:

$$Br_2^0 + 2e^- \longrightarrow 2Br^- \qquad (9\text{-}15)$$

In effect the bromine depolarizes the measuring electrode (gold), allowing copper to go into solution (at the electrode) as electrons flow to replenish the polarizing layer.* The $p$H of the sample is depressed to 4 to convert all the $OCl^-$ to HOCl. This condition provides maximum current flow which is not affected by $p$H variation from 3 to 5. $p$H 4 is optimum for measuring free halogens. In the event that chloramines are present with free chlorine they will also generate a current at the measuring electrode. This interference is on the order of 10 percent of the total combined chlorine residual present. Chloramines will not, however, oxidize any of the bromide ions to free bromine.

The depolarizing current produced by the reactions occurring at the electrode passes through the load resistor. The potential drop across this resistor is directed through the thermistor and millivolt-to-current converter to provide a temperature compensated 4–20 mA DC output signal.

The gold measuring electrode is mechanically connected to the shaft of the motor above the cell which rotates the electrode at 1550 rpm. This helps to maintain ideal, reproducible electrolytic conditions and allows the cell output to be indepen-

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* Free chlorine has always shown a tendency to cause a film-type coating to occur at the surface of the noble metal (Au,Pt) measuring electrodes. This produces a poisoning effect. Free iodine and free bromine do not exhibit this characteristic.

dent of any slight variations in the sample flow rate. Thirty nylon balls are placed in the annular space between the electrodes where their constant motion, maintained by the rotating measuring electrode keeps both electrode surfaces free from foreign matter.

This analyzer is available in selected ranges up to 0–20 mg/l. Accuracy is ±2 percent of range and sensitivity is 0.01 mg/l. Response time is 30–40 seconds upon introduction of sample into sample inlet tank. Cell response is less than 5 seconds full scale.[56] Buffer solution and potassium bromide is pumped into the sample by a peristaltic pump which operates at 1 rpm. Reagent consumption is 0.5 l/day. Sample flow rate through cell is approximately 100 ml/min. Sample to analyzer can be 0.5–3 gpm depending upon local conditions.

*Total chlorine residual* is measured by changing the buffer additive reagent from potassium bromide to potassium iodide. TRC reacts to oxidize the iodide ion to free iodine at $p$H 4. Free iodine generates a current at the measuring electrode in proportion to the TRC.

*Anachlor™ Series 17B4200-2.* This model is a modification of the preceding analyzer. This analyzer was designed for controlling the free residual process which was dependent upon the breakpoint phenomenon.[57,58] This means that the analyzer must be able to distinguish between free and combined chlorine residuals. Morrow and Roop[58] described how they prevented combined chlorine residual interference with the free residual. First they found that chloramine will not oxidize the bromide ion at $p$H 4. Next they examined the separation of the voltammetric curves for free chlorine and chloramines by appropriate applied voltage to the two electrodes. Finally they found a suitable applied voltage that gave sufficient separation of these curves to avoid interference by combined chlorine residual.* This analyzer proved able to perform as described on a wastewater nitrogen removal project at Rancho Cordova California in 1975.[80]

Since this analyzer is identical to the Anachlor Series 17B4200C (described above), except for the external voltage applied to the electrodes, it has the same operating characteristics and requirements.

*Chlor-Trol™ Free Residual Chlorine Analyzer Series 17K/1000.* This analyzer measures free chlorine without the use of any reagents and is supplied with automatic temperature compensation.[59] The amperometric cell consists of two concentrically mounted stationary copper electrodes. A small DC voltage is applied to the electrodes. This causes polarization of the electrodes thereby preventing current flow in the circuit. The presence of free chlorine in the flowing sample depolarizes the electrodes and permits a current to flow in the circuit. This depolarization current is directly proportional to the free chlorine residual concentration in the sample. This current is measured by a series-connected microammeter located within the indicator. The instrumentation contains provisions for zero and span adjustment. Both high and low alarm contacts are also included.

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* See Fig. 9-64.

The range of this analyzer is limited to 0–2 mg/l free chlorine. Accuracy is 0.1 mg/l, and sensitivity is 0.02 mg/l changes in residual. This unit is specific for free residual.* Changes of ±10 percent of sample flow does not affect the cell output. Sample flow through the cell is 750 ml/min (0.2 gpm). Variations in sample water *p*H between 5.0 and 9.0 have no effect on cell performance. Sample water must be free from solids which will not pass through a 170 mesh screen (88 microns) Maximum sample pressure is 40 psi.

*Amperometric Probe.* In 1984 Fischer and Porter was granted a patent (No. 4,441,974) covering a nutating chlorine residual analyzer probe.[84] This probe is unique in the field of chlorine residual measurements. It is a membrane type probe designed for field mounting indoors or outdoors, in open process tanks or channels. It can measure either free or total chlorine residuals without any chemical addition to the sample. The internal chemistry of the probe enables an accurate residual measurement unaffected by pH variations in the process water. It is constantly in motion (nutation). This maintains the integrity of the process sample at the membrane/sample interface preventing depletion of the chlorine species being measured in the region immediately adjacent to the membrane.

The probe illustrated in Fig. 9-68 includes a platinum measuring electrode, an oxidizable silver counter-electrode and an electrolyte which in combination with the electrodes defines an electro-chemical cell. The output current depends upon the amount of chlorine residual passing into the cell through a diffusion membrane permeable to the chlorine species being analyzed. In order to maintain analytical sensitivity of a membrane probe instrument it is highly desirable to simulate rapid sample flow past the membrane. To accomplish this, the probe is vertically supported through a flexible coupling. It contains an internal motor with an unbalanced rotor connected to the shaft of the probe. Rotation of the rotor causes the probe to nutate about its vertical axis. This simulates the effect of rapid sample flow. The nutate or wobble rate is 700–800 cycles per minute.

The internal chemistry of the probe makes use of the reaction between the various chlorine species and bromide salts. Free chlorine reacts with bromide salts to produce free bromine at pH 4.0–4.5. Combined chlorine and bromide salts also react, but at pH levels below 2.0 to produce free bromine. The pH of these reactions is controlled within the probe.

*Free chlorine measurement.* Where this is the chlorine species to be measured the electrolyte within the probe is a concentrated solution of alkali bromide (KBr) buffered to pH 4 with an acetic acid/acetate buffer.

*Combined chlorine measurement.* This measurement does not include free chlorine, only combined chlorine. In this arrangement the saturated solution of potassium bromide is buffered to a pH value approaching zero. It has been found that

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* If chloramine residual develops in the free residual process and it is a small constant amount (10 percent of total residual) it can be calibrated out of the free residual reading.

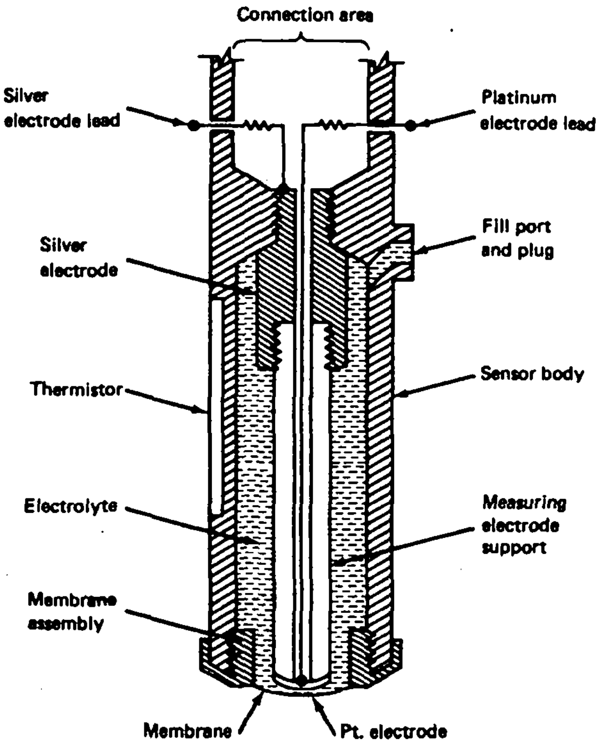

Fig. 9-68. Oscillating probe for a new scientifically advanced amperometric cell (courtesy Fischer and Porter Co.).

at pH levels below 2 the bromine analog signal represents only the combined chlorine species present.

Bromide was chosen rather than the conventional iodide because it avoids the precipitation of insoluble iodide salts within the probe which interferes with the electrode reactions. Furthermore iodide solutions at acidic pH levels undergo auto-oxidation, spontaneously generating free iodine in the solution giving rise to false positive probe currents.

This probe is basically an amperometric device in spite of the fact that a +0.4 Vdc from an external source is applied to the noble electrode. It generates a measurable electric current as a function of the concentration of the species measured. As soon as the chlorine species penetrates the membrane it is reduced to chloride and bromine is generated in proportion to the chlorine residual. Bromine does not contaminate the electrolyte within the probe because it is quickly reduced at the noble electrode back to bromide with a corresponding oxidation of the silver counter-electrode.

$$Br_2 + 2e \longrightarrow 2Br$$

and

$$Ag^0 \longrightarrow Ag^+ + e.$$

Measurement of the resulting current flow shown by these reactions yields a signal proportional to bromine concentration and therefore to chlorine concentration.

An electronic package is associated with the probe. The analyzer displays the residual chlorine concentration on an integral meter and transmits a 4–20 mA signal for remote instrumentation requirements.

The probe has a chlorine concentration range up to 20 mg/l. While no chemicals are required, the manufacturer recommends the electrolyte be changed once every two months. One year of field testing has demonstrated maintenance of the probe is negligible—10 min. every two months to empty and flush the electrolyte reservoir and refill it with the buffered bromide salt solution.

**EPCO: Chlortect® Chlorine Monitor.**[60] This is one of two analyzers based upon the design of the "Flux Monitor" by Marinenko of the U.S. National Bureau of Standards.[61] The other is marketed by IBM (see below). This instrument was designed purposely to detect extremely low levels of chlorine residual in order to determine precisely the toxic effects of total chlorine residuals upon various species of fish and other aquatic life.

This instrument measures total chlorine residual only over a range of 2 ppm. The least amount detectable is claimed to be 2 ppb. The digital display reads from zero to 1000 ppb. Internal calibration is selectable for 1, 10, 100, and 500 ppb.

Two reagents are required: potassium iodide and *p*H 4 buffer. These reagents and chlorinated sample are pumped by their separate peristaltic pumps. There are two cells in the analyzer; one is coulometric and the other is amperometric. The amperometric cell consists of a platinum measuring electrode (cathode) and a nonpolarizable reference electrode (Ag/AgCl) immersed in a salt solution. The coulometric cell consists of a platinum anode and a nonpolarizable reference electrode (Ag/AgCl). The operation of the analyzer utilizes three well established electroanalytical techniques: coulometry, electrolysis, and amperometry. The coulometric cell provides the instrument with internal calibration by electrolytic on-site generation of a known amount of iodine.* This is accomplished by passing a fixed amount of current through the cell (see Fig. 9-69). The magnitude of the current depends upon the calibration range selected and is determined by Faraday's Law of Electrolysis.

The iodine generated by the stoichiometric reaction between the total chlorine

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* A chlorine demand-free sample of deionized water must be available for calibration procedure as shown in Fig. 9-69.

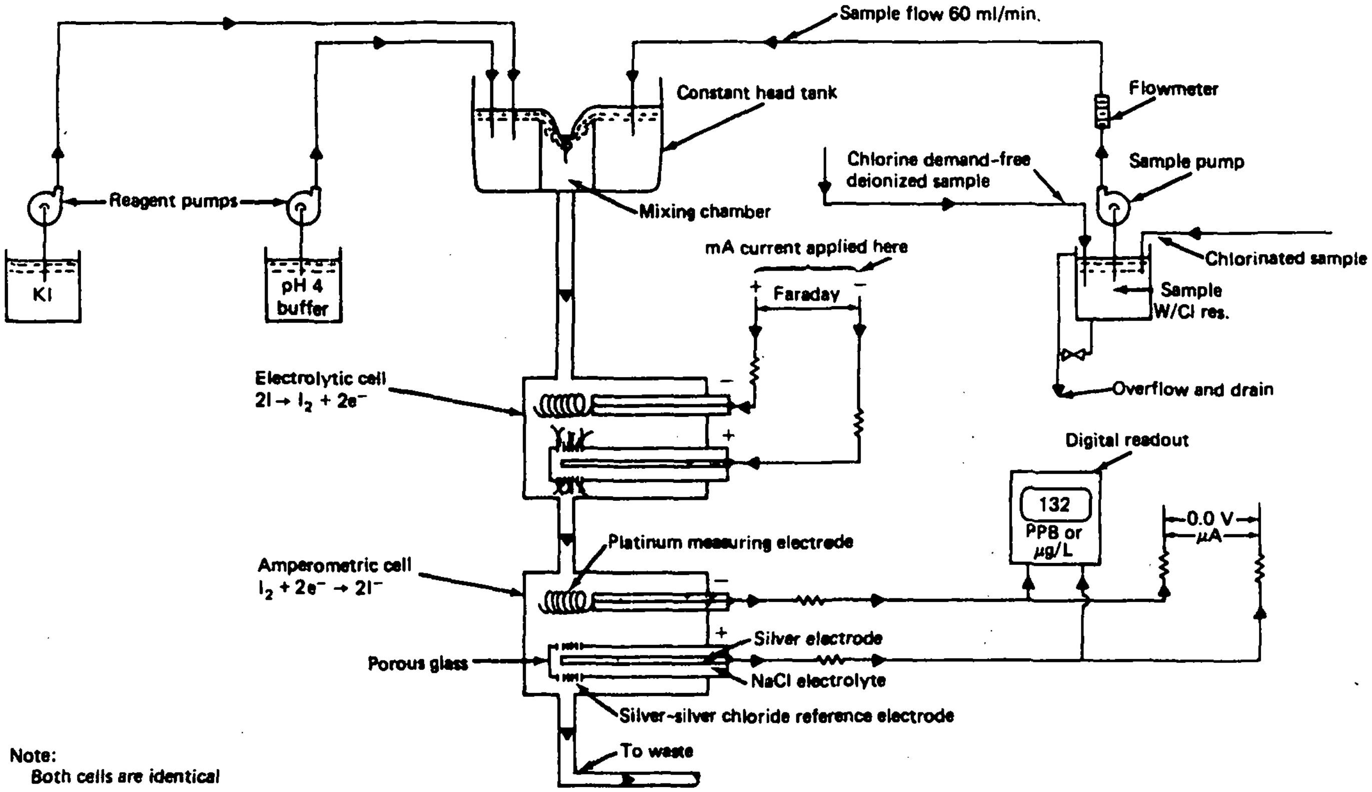

Fig. 9-69. High resolution amperometric cell with internal colometric calibrating circuit utilizing an electrolytic cell (courtesy of EPCO and IBM).

residual in the sample and the potassium iodide added to the sample is measured by the amperometric cell as shown in Eq. 9-16.

$$2\,H^+ + OCl^- + 2I^- \xrightarrow{pH\ 4} I_2 + H_2O + Cl^- \qquad (9\text{-}16)$$

$$I_2 + 2e^- \longrightarrow 2I^- \qquad (9\text{-}17)$$

The current produced by the reduction of $I_2$ to $I^-$ in the amperometric cell is directly proportional to the concentration of $I_2$, which in turn corresponds to the concentration of the total residual chlorine. This amount is displayed directly in ppb or ppm on the digital panel meter.

If any sample preparation is required due to the presence of undesirable foreign matter, the user must assume this responsibility.

**IBM EC/250 Series Chlorine Analyzer.**[62,63] This analyzer is based upon the same principles described above for the EPCO analyzer. These two analyzers have the same schematic arrangement of operation. There are some minor differences. For example model 2A incorporates a heavy duty sample pump and a "self cleaning" filter. Calibration ranges are 10, 100, and 500 ppb; detection limit = 2 ppb; linear range = 10 ppm; accuracy, ±10 percent for linear range; reproducibility ±3 percent; reagent flow rate 1 ml/min; sample flow rate 60 ml/min; and response time 90 percent in 3 min. Optional features are: automatic temperature control, automatic calibration, battery power adapter, high/low alarm and 12 V DC power pack.

**Orion Research.** This manufacturer supplies two chlorine monitors for the continuous analysis of total chlorine residual—only. Model 1570 is for clean water[64] and Model 1770 is for "dirty water."[65] These analyzers use the potentiometric method for the determination of total chlorine residual. This is the only known potentiometric analyzer commercially available at this time (1985).

This method of analysis is based upon detection of the concentration of iodine in the sample using a special electrode. A *p*H buffer is added to the sample to lower the *p*H to between 3.0 and 4.0. KI is then added to the sample to convert all the residual chlorine to iodine. The electrode contains two sensing elements. A platinum electrode develops a potential that depends upon the relative concentration of iodine and iodide in solution:

$$E_1 = E_0 + (S/2)\,(\log\,[I_2]/[I^-]^2) \qquad (9\text{-}18)$$

$$= E_0 + (S/2)\log\,[I_2] - S\,\log\,[I^-] \qquad (9\text{-}19)$$

where

$E_1$ = potential developed by the platinum sensing element, mV

$E_0$ = a cell constant, mV

$S$ = monovalent electrode slope (58 mV/decade at 20°C)

$[I_2]$ = iodine concentration, moles/l

$[I^-]$ = iodide concentration, moles/l

A second electrode, the iodide element, develops a potential that depends upon the iodide ion concentration in solution:

$$E_2 = E_0' - S \log [I^-] \qquad (9\text{-}20)$$

where:

$E_2$ = potential developed by the iodide sensing element, mV
$E_0'$ = a cell constant, mV

The electrode thus measures the difference between potentials developed at the two sensing elements:

$$\begin{aligned} E &= E_1 - E_2 = (E_0 - E_0') + (S/2) \log [I_2] \\ &= E_0'' + (S/2) \log [I_2] \end{aligned} \qquad (9\text{-}21)$$

where

$E_0''$ = potential measured by the analyzer, mV

$E_0'' = E_0 - E_0'$ = a cell constant, mV

The net potential measured by the electrode is converted by analog electronics to read directly as residual chlorine in mg/l. The electrode is calibrated with a standard of known equivalent residual chlorine concentration.

The preceding equations demonstrate that the output of the electrode is proportional to the log of the iodine concentration, and thus proportional to the log of the total residual chlorine concentration. This enables the electrodes to measure the residual chlorine concentration over a 4 decade range from 0.001 mg/l to 10 mg/l.

The only difference between the two models is in the quality of the sample water that is acceptable. Model 1770 is for so-called dirty water and is described here. The sample stream enters the inlet block and the flow is directed at high velocity parallel to the inlet screen. Considerably less than 1 percent of this flow is taken through the screen into the monitor. The surface of the screen is subjected to considerable shear force, which keeps the screen surface clean. This design allows the analyzer to be used on unfiltered samples. The sample then flows to the flow cell block The reagent is passed through a purification column to remove any background iodine, which might have formed during storage, and then is delivered to the block by a separate reagent pump. Sample and reagent are combined within the flow cell block, where they are mixed and agitated by a stream of air. The reagent, which contains sufficient acid to give a resulting *p*H between 3.0 and 4.0 (depending upon the alkalinity of the sample), also contains iodide. The turbulent mixture is directed out of the flow cell block through a mixing loop. Under these conditions, any total residual chlorine reacts completely to form iodine; the resulting iodine concentration is equal to the sample residual chlorine concentration before reaction. The sample then returns to the flow cell block and is directed past a sensing electrode. The turbulence in the mixing loop and agitation against the electrode not only promotes mixing but also helps to minimize fouling of the electrode by sample debris.

Electrode response is affected by sample temperature so automatic temperature compensation circuitry is incorporated in the analyzer.

Specifications for the analyzer claim a sensitivity of 0.001 mg/l, an accuracy and a precision of ±10 percent and ±5 percent, respectively. Note that for precision and accuracy the specifications are stated as a percentage of the actual reading, whereas manufacturers of other residual chlorine analyzers state their specifications for precision and accuracy in terms of percentage of the full-scale reading. The analyzer response time is 2 minutes to obtain a full response from a change in residual chlorine concentration in the sample. Minimum sample flow is 0.5 gal. per minute and minimum allowable water pressure is 20 psi. Maximum allowable is 100 psi.

The manufacturer recommends weekly checks for leaks, replenishment of reagent, and analyzer recalibration monthly. The analyzer is equipped with a sample tap and valve for calibration grab samples. There are no operating data on how often this analyzer must be calibrated for wastewater practice.

**Uniloc, Div. Rosemount Inc.**[66] The Model 852 Chlorine Monitor has been replaced by Model 853. The sensor is Model 450. This analyzer is for measuring free chlorine only. Uniloc does not provide any control instrumentation, but the monitor can provide either current or voltage analog outputs which are compatible with any recorder, controller, or signal converter.

The sensor measures HOCl plus $OCl^-$ but it is blind to combined chlorine. They do not make a unit that measures either combined or total residual chlorine.[67] The analyzer operates on the polarographic principle. A constant 200 mV voltage is applied to a gold cathode and a silver anode. The anode is immersed in an electrolyte chamber of salt solution (NaCl) so that the anode becomes the familiar silver–silver chloride reference electrode. The free chlorine species ($HOCl + OCl^-$) migrate through the membrane between the sample and the electrode chamber. This results in a sensor output current proportional to the free chlorine residual in the sample. The membrane is supposed to have selective diffusion characteristics

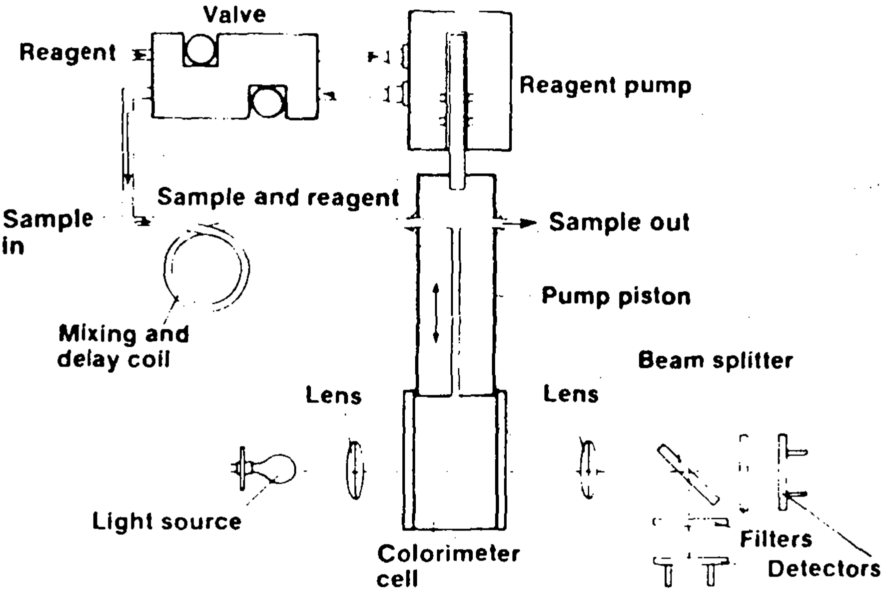

Fig. 9-70. Colometric analyzer showing fluid path and mechanical operation (courtesy Hach Co.).

which allows passage of free residual chlorine species but not combined chlorine. The sensor is temperature compensated.

A four-position range switch permits selection of 0 to 1, 0 to 5, 0 to 10, or 0 to 20 mg/l residual chlorine. High and low alarms with individual adjustable set points are available over the entire range by means of calibrated potentiometers. The alarm set-point can also be displayed on the digital or analog display. Deadband can be adjusted up to 15 percent of full scale.

This analyzer does not require any reagents. The response time in the 0–1 mg/l range is 5 minutes; 0 to 5 mg/l range is 1 minute and 0–10 mg/l range is 30 seconds. Sensitivity is 0.1 ppm at constant *p*H and ±1°C.

**Hach Colorimetric.**[68,69] The Hach company is the only supplier of continuous colorimetric analyzers in North America today (1985). These analyzers use the DPD colorimetric method of analysis. The 31100 model is used to analyze free chlorine over a range of 0–2 mg/l. The 61100 model covers a range of 0–5 mg/l. The 31300 model is designed to analyze total chlorine residual.

Figure 9-70 shows the basic mechanical operation and fluid path of sample and reagent through these analyzers. The reagent pump and sample pump pistons are synchronized precisely so that the reagent is added simultaneously with the sample. As the sample piston rises, drawing the sample in, the reagent piston discharges reagent into the sample stream. A mixing and delay coil provides time

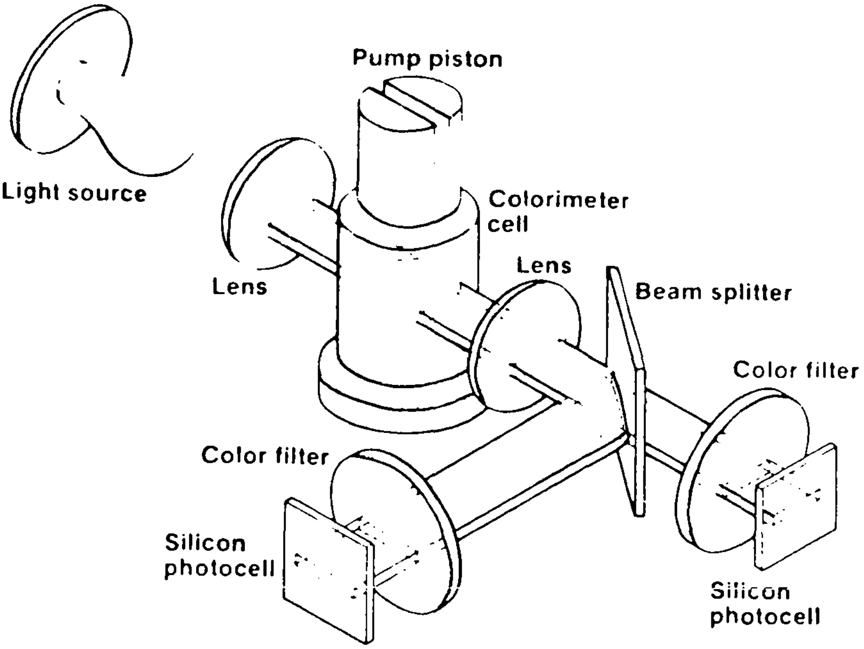

Fig. 9-71. DPD colorimetric analyzer, optical design (courtesy Hach Co.).

for the sample and reagent to completely mix and the colorimetric reaction to progress to completion before the sample enters the colorimetric cell. After analysis (the other half of the pump cycle) the sample pump discharges while the reagent pump draws in the next portion. Valves (not shown in Fig. 9-70) open and close during the parts of the cycle when the pistons are stationary.

Figure 9-71 shows the optical design of the analyzers. The light beam passes through a lens before entering the cylindrical pump/sample cell. After passing through the cell, the light encounters a beam splitter, which directs part of the beam through a filter to a reference detector located at 90° to the light path. The other, main part of the light beam passes through a filter to a sample detector. The signals from the two detectors are fed to the electronics package for processing. The single-beam/dual-wavelength capability provides a correction for any changes in light source or sample cell condition, and can compensate for moderate changes in sample turbidity and color by the reference wavelength used in the analyzer. Although these features increase the reliability when the analyzer is used to determine residual chlorine concentrations in wastewaters that may contain suspended solids and other contaminants, sample pretreatment is still required for removal of debris and large solids which may foul or plug the analyzer.

A block diagram of the analyzer electrical system is shown in Fig. 9-72. Light, after passing through the sample, strikes the reference and sample silicon photocells.

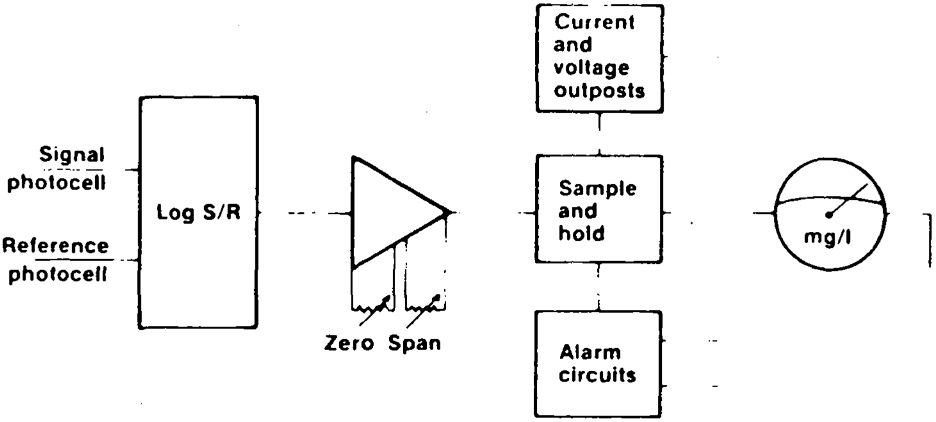

Fig. 9-72. DPD colorimetric analyzer, block diagram of electrical system (courtesy Hach Co.).

This produces a current, which goes to a log-ratio converter. The converter sends out a signal equal to the log of the ratio between the two currents. The log-ratio signal travels to an amplifier with gain and offset controls and then to a sample-and-hold circuit. A microswitch is activated when the sample piston is at the top of the cylinder/sample cell (allowing an unobstructed light path). This advises the sample-and-hold circuit to put the amplifier output into storage. The meter and other external readouts indicate this value, which is stored until the next cycle.

Free available chlorine DPD colorimetric analyzers are available with one of four factory-preset ranges. The widest range is 0–5.0 mg/l. Total residual chlorine DPD colorimetric analyzers are available with one of three factory-preset ranges. The widest range is 0–2.0 mg/l. The analyzers have no automatic temperature compensation. The effect of varying sample temperatures or ambient temperature can be significant.[52] Hach offers an optional sample heater which will maintain the sample temperature within ±1.5°C. This should be included as an integral part of these analyzers.

A major drawback of these analyzers is the response time to variations in sample concentrations. Unlike other analyzers, the concentration is determined using discrete samples. One complete sample cycle requires time for entry of the sample into the analyzer, addition of reagent, color development, and expulsion of the sample from the analyzer. The supplier's specifications state the following response times:

| | |
|---|---|
| Free available chlorine | Initial response in 30 seconds,<br>97% in 2 minutes |
| Total residual chlorine | Initial response in 5 minutes,<br>95% response in 7 minutes |

This response time is unacceptable for either residual control or the dechlorination process. These analyzers are relatively insensitive to drift, as demonstrated by the following supplier specification:

> A drift rate of less than 0.5 percent of full scale over 24 hours when measuring 0 mg/l residual chlorine with a constant sample temperature of 25°C and a constant ambient temperature of 30°C.

The sensitivity claimed by Hach is 0.02 mg/l, precision is ±0.5 percent of full scale at constant ambient and sample temperature, and accuracy is ±5 percent for the same conditions.

It is unlikely that these analyzers could be used for anything other than monitoring.

## HOUSING

**General.** Many important design provisions for chlorination housing relate to the safe use of chlorine and the protection of those working with it. Consequently, many chlorine room design provisions are required elements of state standards.

Chlorinator and sulfonator rooms should be at or above ground level. Container storage should be planned so that it is separate from chlorinators and accessories. It is logical to locate the chlorination room near the point(s) of application to minimize the length of chlorine lines. Other general site considerations include a location which permits ease of access to facilitate container transport and handling, adequate drainage, and separation from other work areas.

**Separation.** Proper design standards require either a completely separate chlorination building or a room completely separate from the remainder of the building with access only through an outside door. There should be no apertures of any type from the chlorination room to other parts of a common building through which chlorine gas could enter other work areas.

**Fire Hazard.** The building should be designed and constructed to protect all elements of the chlorine system from fire hazards. If flammable materials are stored in the same building, a fire wall should separate the two areas. Fire-resistive construction is recommended. Water should be readily available for cooling cylinders in case of fire.

**Space Requirements.** Modern chlorination equipment is available in modules so that the chlorinators and accessory equipment can be arranged in a panel-like array. There should be about four feet between the front of a module and the nearest wall and about two feet on the sides and rear. Fig. 9-11 illustrates space requirements for chlorinator–evaporator installations and Fig. 9-14 illustrates space requirements for a ton container supply area.

The smallest area used for the installation of a chlorinator, weighing scales, and a spare cylinder* of chlorine should not be less than 6 feet by 6 feet.

There should be adequate room provided to allow ready access to all equipment for maintenance and repair. There should be sufficient clearance to allow safe handling of equipment containers. Absolute minimum clearance around and in back of equipment is 2 feet.

Some general minimum space guidelines are as follows:

1. Plants with one chlorinator feeding less than 200 pounds per day should have at least 64 square feet.
2. Plants using two chlorinators with a total feed rate of up to 400 pounds per day should have at least 160 square feet.
3. For each chlorinator–evaporator unit, 160 square feet should be provided.

**Ventilation.** Adequate forced air ventilation is required for all chlorine equipment rooms. An exception to this would be small chlorinator installations (<100 pounds per day) located in separate buildings if the windows and doors can provide the proper cross-circulation. For a small building, windows in opposite walls, a door with a louver near the floor, and a rotating-type vent in the ceiling usually provide the necessary cross-ventilation.

Factors to be considered in the design of a ventilation system are: air turnover rate, exhaust system type and location, intake location and type, electrical controls, and temperature control.

A forced air system should be capable of providing one complete air change in 2–5 minutes. Since chlorine gas is 2½ times heavier than air, it is logical to provide air inlet openings for ventilation fans at or near floor level. For small installations it is common to employ an exterior exhaust fan with the intake duct extending to the chlorine room floor. A wall-type exhaust fan is an acceptable alternative. The exhaust system should be completely separate from any other ventilation system. For larger installations a blower-type fan is needed. The use of free-moving, gravity-operated louvers may be advantageous in colder climates for conserving room heat when the blowers are not in operation; however, venting systems should not have covers. The fan discharge should be located so as to not contaminate the air supply of any other room or nearby habitations. It is mandatory that the ventilation discharge be located at a high enough elevation to assure atmospheric dilution, e.g., at the roof of a single-story building.

Air inlets should be so located as to provide cross-ventilation. To prevent a fan from developing a vacuum in the room and thereby making it difficult to open the doors, louvers should be provided above the entrance door and opposite the fan suction. In some cases, it may be necessary to provide temperature control on the air supply so that the chlorination system is not adversely affected. A

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* This space is for chlorination systems using a 150 lb cylinder

signal light indicating fan operation should be provided at each entrance when the fan can be controlled from more than one point.

**Wind Socks.** All installations should locate at least one wind sock on the chlorine supply structure. This is very valuable in the event of a leak.

**Doors.** Exit doors from the chlorination room should be equipped with emergency hardware and open outward. Some design guides recommend two means of exit from each room or building in which chlorine is stored, handled, or used; however, this would not appear to be essential in most cases.

**Inspection Window.** A means should be provided which permits viewing of the chlorinator and other equipment in the chlorination room without entering the room. A clear glass, gas-tight window which is installed in an exterior door or interior wall of the room is recommended. Door windows appear to be a logical provision even with a separate wall inspection window.

**Heating.** The chlorinator room should be provided with a means for heating and controlling room air temperatures above 55°F. A minimum room temperature of 60°F has been recommended as a good practice. Ideally, the heating system should be able to reliably maintain a uniform moderate temperature throughout the chlorination room.

Hot water heating is generally preferred because of safety considerations and the uniformity of temperature which this method of heating provides, without the extremes which might be experienced with failure of a steam heating system. Electric heating is suitable and forced air heating would be appropriate if an independent system is provided for the chlorination room or building. Central hot air heating is not acceptable since gas could escape through the heating system.

Chlorine vapor leaving a container will condense if the piping temperature is significantly lower than the temperature of the container. Design should provide a higher temperature in the chlorinator room than in the container room. This applies to systems using the gas phase from the containers. Elimination of unnecessary windows may aid in maintaining uniform building temperatures.

If container storage and chlorination equipment are in separate rooms, the temperature of the chlorine container should not be allowed to drop below 50°F *if evaporators are not used.*

**Drains.** It is generally desirable to keep the plant floor drain system separate from that of the chlorinator. Drainage from a chlorinator drain relief valve may contain chlorine. Consequently, hose, plastic pipe, or tile drains are recommended. The discharge should be delivered to a point beyond a water-sealed trap or disposed of separately where there is ample dilution.

Scale pits are generally designed with floor drains having a water-sealed trap.

In actual practice, most traps probably do not contain enough water to form a seal and it would be preferable to provide a straight pipe drain outside to grade.

**Vents.** Chlorinators, external chlorine pressure reducing and shutoff valves, remote vacuum systems, and automatic switchover systems have vents. Chlorinators have a pressure vacuum relief system which should be carried to the outside atmosphere without traps to a safe area, with one vent for each chlorinator. In the case of a malfunction, the operator can easily determine which chlorinator is malfunctioning if the vents are separate. The ends of the vent lines should point down, be covered with copper wire screen to exclude insects, and should not be more than 25 feet above the chlorinator. The line should have a slight downward pitch from the high point (directly above the chlorinator) to drain any condensate away from the chlorinator. It is acceptable to run the vent vertically (but no more than 25 feet) above the chlorinator to the roof, with a 180° return bend at the exit.

External chlorine pressure-reducing and shutoff valves should be checked for vents. When supplied, these vents should drain away from the valves. In other words, these valves should be located high enough so that the individual drains will have a continuous downgrade to the outside atmosphere.

Manufacturer's instructions should be followed for vents required with remote vacuum and automatic switchover systems. Evaporators* have water bath vapor vents which can be manifolded together and discharged to the atmosphere without traps.

**Electrical.** Controls for fans and lights should operate automatically when the door is opened and there should be provisions to activate these manually from outside the room. Switches for fans and lights should be outside of the room at the entrance. A signal light indicating fan operation should be provided at each entrance when the fan can be controlled from more than one point.

## RELIABILITY PROVISIONS

The need for continuous and dependable disinfection has been stressed. The chlorination system can fail due to a number of causes and, therefore, the design of the system must include the necessary provisions to either prevent failures or allow immediate corrective action to be taken. Although assured reliability is essential, design provisions for this are often slighted.

**Chlorine Supply.** As a chemical feed process, one of the most frequent interruptions in treatment is caused by the exhaustion of the chlorine supply. Five features are essential to maintain continuous chlorine feed: (1) an adequate reserve supply

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* Evaporator relief system vents require special consideration for local conditions

of chlorine sufficient to meet normal needs and bridge delivery delays and other possible contingencies; (2) chlorine container scales; (3) a manifolded chlorine header system; (4) an automatic device for switching to a full chlorine container when the one in use becomes empty; and (5) an alarm system to alert operating personnel of imminent loss of chlorine supply. These five features are discussed elsewhere in this text. Without them it is not possible to assure uninterrupted chlorine feed even with full-time operator attendance and no equipment breakdowns.

The chlorine header system is needed both to provide a connected on-line chlorine supply which is adequate to assure uninterrupted flow of chlorine for whatever period that the system may be unattended and to allow switchover to a full cylinder without interruption of chlorine.

**Power Failure.** Power outage usually results in water supply failure which in turn automatically shuts down the chlorination system. A range of special provisions can be employed to assure reliability of power and water supply depending upon the particular situation. As discussed previously, these may be in the form of a standby power source and pumps.

**Standby Equipment.** The design of the chlorine feed system should provide for continued operation in cases of equipment failure. Where both pre- and postchlorination are to be practiced, separate chlorination systems should be provided for each plus a standby system. If prechlorination is not to be continuously used, it may be possible to use this system as the standby system for disinfection. The units, piping, and accessories should be designed with this application in mind. If prechlorination must be carried out continuously or if no prechlorination is to be done, a standby system, capable of replacing the postchlorination system during repairs, maintenance or emergencies should be provided. Standby equipment of sufficient capacity should be available to replace the largest unit during shutdowns. This includes standby pumps for the injector water supply.

In addition to standby equipment, the equipment manufacturer should be consulted regarding vulnerable components. These components should be a part of the plant's inventory of spare parts.

**Water Supply.** As mentioned above, during a power failure the injector water system will be shut down unless there is an alternate supply that does not require power, such as an elevated tank. Standby equipment to provide injector water in the event of a power failure would consist of an engine driven injector supply pump. Every injector water supply system should have such a standby pumping unit. There is no way to operate the chlorination system without an adequate water supply.

**Chlorine Residual Analyzers.** Every system using an analyzer for chlorination control should be backed up by an effluent monitor analyzer that can be switched over to the control function in the event of control analyzer failure. Similarly, backup capability should be provided for analyzers controlling and monitoring the dechlorination process. Provisions should be made for standby sample pumps. Sample lines should be piped to facilitate flushing or purging to remove biological slimes.

## AMMONIATION FACILITY

### AMMONIA—$NH_3$

**Useful Ammonia Compounds.** Ammonia is commercially available in four forms: anhydrous ammonia, $NH_3$, commonly stored and transported as a liquid in pressure vessels; aqua ammonia, $NH_4OH$, most commonly a 20–30 percent solution of ammonia in deionized or softened water; white crystalline ammonium chloride, $NH_4Cl$, very soluble in water; and ammonium sulfate, $(NH_4)_2SO_4$, a gray-green crystalline solid which is hygroscopic. The latter two must be dissolved in water to be useful in waterworks practice.

**Source, Availability and Uses.** Ammonia, $NH_3$ does not appear free in nature. It occurs in compounds as the $NH_4^+$ ion. However, the primary source for the nitrogen atom is in the atmosphere. All ways to make ammonia consist of combining one atom of nitrogen with three atoms of hydrogen.

Ammonia is extremely important commercially. Its most notable uses are for refrigeration and fertilizers. Other uses include explosives, petroleum refining, rubber, textiles, chemicals, pulp and paper, and metallurgy. It is a byproduct of the destructive distillation of coal and coke, but most of the ammonia produced in the United States is by the Haber process. This process produces ammonia by direct synthesis. Gaseous nitrogen and hydrogen are mixed in correct proportion and heated under pressure (up to 1000 atm.) at 400–600°C and passed over a catalyst. The pure nitrogen for the process is obtained from liquid air, while natural gas (methane, $CH_3$) is the usual hydrogen source. This is why oil companies are usually the important suppliers of ammonia. For example, Union Oil Co. is the main supplier on the West Coast of U.S.A. owing to their participation in the Alaska Pipeline. They have an ammonia manufacturing plant in Kenai, Alaska. From here it is shipped to West Coast ports and exported to Far East countries.

About 30 billion tons of ammonia are produced annually in the U.S.A. Its production is exceeded only by sulfuric acid and oxygen.

**Physical and Chemical Characteristics.** Ammonia is a colorless gas with a very pungent, irritating odor. However, when it is released into the atmosphere it creates a rather dense white fog. This is due to its immediate reaction with the moisture in the atmosphere. Ammonia is highly soluble in water

At normal temperatures and pressures anhydrous ammonia is a gas. It is easily liquified by pressurizing in a container and it is commonly stored and transported as a liquid. When the liquid reverts to a gas a great amount of heat is absorbed. This is why it is extensively used for refrigeration.

At atmospheric pressure liquid ammonia has a density of 42.6 lb/ft$^3$, approximately two-thirds that of water. The vapor pressure of ammonia at 70°F is 114 psi compared to chlorine at 85 psi (see Fig. 12, Appendix). The important properties of ammonia are shown in Table 9-10.

Table 9-10 Physical Properties of Ammonia[70]

| | |
|---|---|
| Molecular symbol | $NH_3$ |
| Molecular weight | 17.031 |
| Boiling point at 1 atmosphere* | −28°F (33.3°C) |
| Freezing point at 1 atmosphere | −107.9°F (−77.7°C) |
| Critical temperature | 271.4°F (133.0°C) |
| Critical pressure | 1657 psia (114.2 bars) |
| Latent heat at −28°F (−33.3°C) and 1 atmosphere | 589.3 Btu/lb (13.71 × $10^5$ J/kg) |
| Relative density of vapor compared to dry air at 32°F (0.0°C) and 1 atmosphere | 0.5970 |
| Vapor density at −28°F (33.3°C) and 1 atmosphere | 0.0555 lb/ft$^3$ (0.8899 kg/m$^3$) |
| Specific gravity of liquid at −28°F (−33.3°C) compared to water at 4°C | 0.6819 |
| Liquid density at −28°F (−33.3°C) and 1 atmosphere | 42.57 lbs/ft$^3$ (681.9 kg/m$^3$) |
| Specific volume of vapor at 32°F (0.0°C) and 1 atmosphere | 20.78 ft$^3$ (1.297 m$^3$/kg) |
| Heat of solution at 0% conc. by wt. | 347.4 Btu/lb (8.081 × $10^5$ J/kg) |
| Heat of solution at 28% conc. by wt. | 214.9 Btu/lb (4.999 × $10^5$ J/kg) |

* atmosphere = 760 mm Hg = 1.01325 bars.

## Characteristics which Affect Use in Water Treatment:

*Weight.* Molecular weight of ammonia (17.03) is half that of chlorine (35.5). Therefore a 2000 lb/day chlorinator can only feed 950 lb/day ammonia.

Ammonia gas is lighter than air, so leaking vapor will rise quickly; in contrast, chlorine, which is heavier than air, tends to settle toward the ground.

*Heat of Vaporization.* Nearly 5 times that of chlorine. Therefore, a 10,000 lb/day chlorine evaporator can vaporize only 2,000 lb/day ammonia.

*Solubility in Water.* Almost 50 times that of chlorine. This simplifies the requirements for mixing at the point of application and reduces significantly the quantity of injector water required. This minimizes the burden when injector water must be softened to a hardness not exceeding the solubility of calcium carbonate (35 mg/l).

*Reaction with Water.* 1 mg/l $NH_3$ will *increase the alkalinity* of water by 2.9 mg/l (as $CaCO_3$), whereas 1 mg/l chlorine reduces the alkalinity 1.4 mg/l.

*Corrosivity.* Dry ammonia, either liquid or gas is not corrosive to any metals. Moist ammonia will not corrode iron or steel but will react (to corrode) with copper, brass, zinc and most copper alloys. Never use galvanized pipe. Valves, flex connections, and other hardware used in chlorine supply systems contain pure copper and/or copper alloys—therefore they are not interchangeable with comparable ammonia supply hardware.

*Water Softening Reaction.* This is the one and only disadvantage of ammonia use in water treatment. Ammonia reacts with the hardness in water to produce a softening effect comparable to excess lime softening. This occurs at the interface between ammonia vapor and water: at the inlet to the injector throat and at the exit of the direct feed gas diffuser. At these two interfaces a scale will develop directly in proportion to the calcium and magnesium hardness. Stoppage occurs quickly due to this scale. This is why all injector water should be softened to the maximum solubility of calcium carbonate (35 mg/l). For the direct feed diffuser, the one supplier of this equipment solved the hardness problem with a diffuser design modification many years ago.

**Physiological Effects.** Persons having chronic respiratory disease or persons who have shown evidence of undue sensitivity to ammonia should not be employed where they will be exposed to ammonia.

Ammonia is not a cumulative metabolic poison; however, ammonia in the ambient air has an intense irritating effect upon the mucous membranes of the eyes, nose, throat, and lungs. High levels of ammonia can produce corrosive action on these tissues which can cause laryngeal and bronchial spasms, as well as edema which will obstruct the breathing passages. Conscious people are protected by its pungent odor, but unconscious people are not. Table 9-11 lists human physiological response to various concentrations of ammonia in air. It should be noted here that individuals differ in their sensitivity to ammonia. Some are highly reactive to low concentrations while others show a significant tolerance to the irritative effects.

## SUPPLY SYSTEM: ANHYDROUS AMMONIA

**Cylinders.** Two sizes, 100 lb and 150 lb, are usually available, but not as common as they were. Cylinders are equipped with a dip tube so that when they are placed horizontally, liquid can be withdrawn.

### Table 9-11 Physiological Response to Ammonia[70]

| | Concentration, ppm |
|---|---|
| Least perceptible odor | 5 |
| Readily detectable odor | 20–50 |
| No discomfort or impairment of health for prolonged exposure | 50–100 |
| General discomfort and eye tearing; no lasting effect on short exposure | 150–200 |
| Severe irritation of eyes, ears, nose, and throat; no lasting effect on short exposure | 400–700 |
| Coughing, bronchial spasms | 1,700 |
| Dangerous, less than ½ hour exposure may be fatal | 2,000–3,000 |
| Serious edema, strangulation, asphyxia, rapidly fatal | 5,000–10,000 |
| Immediately fatal | 10,000 |

**800 lb Container.** These are still available but are not as popular as bulk storage tanks. They are similar to chlorine ton cylinders. They are equipped with dip tubes for vapor or liquid withdrawal and are the same physical size as chlorine ton containers. Therefore a chlorine ton container lifting bar and trunnions will fit these cylinders.

### Storage Tanks:

*General Consideration.* Bulk storage tanks sized to fit the consumer's needs are the most popular means of on-site ammonia storage. For example, in the Southern California area the Union Oil Co., Chemical Division, has a large fleet of 8000 gallon tank trucks used to service customer storage tanks on a routine basis. USS Agrichem (U.S. Steel Co.) and Chevron provide similar service in other areas.

Consumers in the water treatment industry are advised to purchase refrigeration grade ammonia instead of commercial grade because it is moisture free. Commercial grade ammonia purposely contains a small amount of moisture to reduce stress fractures (fatigue). This prolongs tanker life.

*Design Factors.* It is common practice in the industry for the supplier to build or furnish the consumer with a storage tank. Certain features should be a part of a proper storage tank. The shell should be designed for at least 250 lb working pressure.[70] There should be one liquid outlet with an excess flow check valve inside the tank and two vapor outlets, all with stainless steel trim shutoff angle valves (similar to a chlorine tank car). In the vicinity of these valves there should be a safety relief valve with a vent line which discharges 2–3 feet above "roof" height. It should end in a double 90 degree elbow to prevent rain from entering the vent and it should have a moisture trap-leg adjacent to the valve discharge. This moisture trap will eliminate moisture interference with the relief valve.

*Filling Density.* The allowable filling density for uninsulated stationary storage tanks is 82 percent by volume and 56 percent by weight. Therefore an integral part of the storage tank must be a device to measure the weight or volume of ammonia at any time.

*Inventory Control.* The preferred method of determining the status of ammonia supply is by weight. Therefore the contents of the tank should be weighed by either a set of industrial lever-type scales or a load cell. A load cell with a 4–20 mA signal for remote display is preferable to scales.

*Withdrawal Rates.* This is an important factor when selecting the size of a storage tank. Assume that the maximum withdrawal rate will never exceed 1000 lb/day and assume that this much vapor will be needed at an ambient temperature of 50°F. How big will the storage tank have to be? The formula for withdrawal rates for ammonia is as follows:[2]

$$[\text{Room temp}(°\text{F}) - \text{Liquid temp } (°\text{F})] \times \text{withdrawal factor} = 1000 \text{ lb/day}$$

Liquid temperature is the temperature of the ammonia at minimum allowable inlet pressure to the ammoniator (10 psi). This pressure is required to actuate the remote vacuum regulator. At 10 psi the liquid temp is −5°F. Let the withdrawal factor be $W$:

$$[50 - (-5)]\ W = 1000 \text{ lb/day}$$

$$W = \frac{1000}{55} = 18.2$$

An 800 lb cylinder (192 gal) has a withdrawal factor of 3.2:[2]

$$\frac{\text{W}}{192} = \frac{18.2}{3.2}$$

$$= 1094 \text{ gal}$$

Therefore an 1100 gallon tank when full could provide a 1000 lb/day vapor withdrawal rate at 50°F ambient temperature.

**Evaporators.** Ammonia evaporators are identical to chlorine evaporators* but they must not be used interchangeably because this practice could produce an

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* Except that inlet and outlet valving have 316 SS trim.

explosive mixture of chlorine and ammonia. The major difference between chlorine and ammonia evaporators is capacity. A 10,000 lb/day chlorine evaporator can only vaporize 2,000 lb/day ammonia.

Evaporators for ammonia are being used in water treatment practice where the ammonia is supplied in 800 lb cylinders. Evaporators can and should be avoided by the use of custom-made storage tanks.

**Leak Detectors.** As of 1985 continuous leak detector monitors similar to chlorine detectors are not available. However American Gas and Chemical Co. of Northvale, NJ market the following products for locating ammonia leaks at the source.

Their aerosol powder, ADP-219, can be sprayed onto areas of suspected leaks (pipe joints, fittings, valves, etc.) as a yellow powder coating which changes to a dark blue in the presence of a small leak. The coating can easily be removed with a damp cloth.

Another aerosol spray, ADS-100, generates white smoke upon contact with ammonia fumes. This spray tends to neutralize the escaping ammonia, making it less hazardous, and produces a visible fog which grows more intense as it approaches the leak.

Their CG Tracer is a small, hand-held device sensitive to both ammonia and combustible gases. It can quickly locate an ammonia leak.

**Potential Hazard of a Major Leak.** There are two physical properties of anhydrous ammonia that reduce significantly the hazard of a major leak. These factors can be graphically illustrated by the events of a recent major leak. A Chevron tanker truck overturned in Richmond, California, resulting in a 6 inch gash in the tank shell. The Chemtrec emergency response team arrived to see a dense white fog rising into the atmosphere above the overturned truck.[73] Fire hoses were sprayed into the fog (ammonia plus atmospheric moisture) which disappeared immediately upon contact with the water. This is the result of the high solubility of ammonia in water. Ammonia is so much lighter than air that it rises quickly above and beyond people at ground level, which is greatly different from chlorine. After the fog was washed into the storm drains, water was sprayed into the gash on the tank. By this time the vaporization of the liquid due to the leak, cooled the liquid sufficiently so that the water formed an ice cover which sealed off the liquid ammonia long enough to right the truck and move it to a safe place where it was emptied without further incident. The high latent heat of vaporization of liquid ammonia is directly responsible for the rapid formation of the ice cover. This is the characteristic which makes ammonia a universal refrigerant. From the above accident description it can be seen that ammonia is a relatively safe gas. Furthermore, the levels of concentration required to produce a dangerous environment are many more times those for chlorine or sulfur dioxide

**Materials of Construction.** The supply system under pressure should be Sch 80 seamless steel pipe with 3000 lb forged steel fittings. Welded joints are preferred

Use bell reducer-type fittings. Bushings should never be used. Unions should be 2-bolt flanged with a lead gasket joint. Valves should be steel with 316 stainless steel trim.

All ammonia piping under a vacuum should be Sch. 80 PVC with solvent weld joints.

## AMMONIATORS

**Direct Feed.**[71] This type of ammoniator is available from only one manufacturer as of 1984 (Wallace and Tiernan). Metering capacities up to 1000 lb/day are available. All sizes come equipped with a special diffuser designed to prevent interference from scale formation and back-flooding of the equipment The pressure at the point of application *must not exceed 15 psi.*

The manufacturer advises that there were over 200 direct-feed ammoniators in operation in 1984. Because of their stainless steel construction and the characteristics of ammonia there are no corrosion problems, hence they are rugged, low-maintenance devices. White recently observed a pair of these units in operation for nearly 50 years.

The direct feed unit can be furnished for either manual control or automatic flow-paced control. The automatic version costs about three times as much as the manual unit. Operating experience with the automatic type has proved to be satisfactory.

### Solution Feed[72]:

*General Description.* Solution feed ammoniators are available from the top three chlorinator manufacturers. They are identical in design to chlorinators and sulfonators except for minor differences in materials of construction to conform to the chemical characteristics of ammonia vapor and aqueous solution. They are available up to capacities of 950 lb/day and are usually arranged for remote vacuum operation. Automatic switchover components are optional. The major design difference is in the sizing of the injectors, which is described below.

*Control Strategies.* Ammonia should be applied at a fixed ratio to chlorine for the best and most consistent results. Hence the ammoniator should be controlled by the same signals which control the chlorinator. The precise ratio of ammonia to chlorine can be achieved by rotameter feed-rate selection and use of the manual dosage adjustment on the ammoniator.

### Injector System:

*Water Requirements.* The major disadvantage of a solution-feed ammoniator is the softening reaction caused by the formation of ammonium hydroxide:

$$NH_3 + H_2O \longrightarrow NH_4OH \tag{9-22}$$

The ammonium hydroxide precipitates the calcium and magnesium hardness down to the solubility limit of $CaCO_3$, which is 35 mg/l. Therefore the injector water should be softened to this level of hardness to prevent the injector from plugging due to hardness scaling.* Owing to the high solubility of ammonia in water, much less water is required for solution feed ammoniators than for chlorinators. For example, one manufacturer requires only 4.25 gpm with 50 psi injector water for 240 lb/day ammonia versus 6 psi back-pressure and only 2.5 gpm versus 2 psi back-pressure.[73] Therefore the manufacturer should be consulted early to determine injector water requirements, particularly if softening is to be involved.

The above figures are based upon the use of 1-inch fixed-throat injectors which are limited in ammonia capacity to 240 lb/day. Multiple injectors are required to achieve a maximum capacity of 950 lb/day. In any case, duplicate injectors and duplicate diffusers are recommended for solution feed ammoniators.

*Vacuum Lines.* Sizing of these lines is critical owing to the use of remote vacuum and remote injectors. The following analysis will serve as an example of the necessary calculations using these formulae:

Head loss in vacuum line:

$$\Delta P \text{ (in. Hg)} = \frac{11.89 \times L \times f \times W^2}{10^9 \times p \times d^5} \tag{9-23}$$

where

$L$ = equivalent pipe length, ft

$f$ = friction factor (see Figs. 10 and 11, Appendix)

$W$ = lb/day ammonia

$p$ = density of $NH_3$, lb/ft$^3$

$d$ = pipe diameter, inches

Reynolds number:

$$N_R = \frac{6.32 \times W}{\mu \times d \times 24} \tag{9-24}$$

---

* Capital Controls announced (1984) a special solution-feed ammonia injector with a flexible liner timed to flex by external water pressure on a programmed basis. The flexible liner is intended to shred the hardness scale buildup

where

$W$ = lb/day ammonia

$\mu$ = viscosity of $NH_3$, centipoise
$d$ = pipe diameter, inches

Use the Reynolds number to select the friction factor from Fig. 8, Appendix. Calculate the density of ammonia at 20 in. Hg vacuum and 50°F:

$$PV = NRT \tag{9-25}$$

where

$P = -20$ in. Hg or $(30-20)/30 = 10/30$ atm. $= 0.33$ atm.

$T$ = 50°F or 283°K

$R = 0.08205$

Hence

$$0.33V = (0.08205)(283)$$
$$V = 70.36 \text{ l/mole}$$

$$17.03 \text{ g/mole} \times \frac{1 \text{ mole}}{70.36} \times \frac{1 \text{ lb}}{454 \text{ gm}} \times \frac{28.3 \text{ l}}{\text{ft}^3} = 0.015 \text{ lb/ft}^3$$

Therefore

$$p = 0.015 \text{ lb/ft}^3 \text{ at 20 in. Hg and 50°F}$$

Solve for Reynolds number using viscosity of $NH_3$ at 0.0095 centipoises at 50°F. Try 1.25 inch pipe and use max. capacity of the ammoniator (950 lb/day):

$$N_R = \frac{6.32 \times 950}{0.0095 \times 1.25 \times 24}$$
$$= 21{,}066$$

$f$ from Fig. 8 (Appendix) is 0.03.

Now solve for total head loss in 300 ft of pipe using Eq. (9-23):

$$\Delta P = \frac{11.89 \times 300 \times 0.03 \times (950)^2}{10^9 \times 0.015 \times (1.25)^5}$$
$$= 2.11 \text{ in. Hg}$$

Therefore a 1.25-inch diameter PVC pipe is borderline, so use 100 ft of 1.5-inch and 200 ft of 1.25-inch.

### Diffusers and Solution Lines:

*Mixing.* The solution lines should be sized so as to not exceed 1.5 ft total head loss. The diffusers should be designed with holes that will create a head loss of 8–11 ft. This will translate to a $G$ factor of 250–300, which is sufficient turbulence for a quick mix. The orifice jets must point upstream.

*Back-Pressure.* The injector should be located as close to the diffuser as possible, which in nearly all instances calls for a remote injector. The centerline of the injector throat should be above the hydraulic gradient of the plant in order to keep the back pressure as low as possible. If it is not practical to keep the back pressure below 10 psi (to minimize injector water consumption) the ammonia solution should be pumped with a small turbine pump. Optimum back pressure is about 2 psi.

*Contact Time.* The reaction of ammonia nitrogen with chlorine to form chloramines is practically instantaneous, so contact time is not a factor—rapid dispersion of the ammonia solution is the principal factor.

*Flushing.* Diffusers should not only be provided in duplicate, they should be arranged so that they can be flushed with acid or chlorine solution to dissolve any formation of carbonate scale.

## ADVANTAGES OF SOLUTION FEED ANHYDROUS AMMONIA

A great many chloramine systems in the U.S.A. use ammonium hydroxide solution. When faced with a decision to select aqua or anhydrous ammonia, Engineering Science, consulting engineers, Pasadena, CA conducted a survey of both forms and concluded that anhydrous ammonia was more advantageous for the following reasons:[74]

- Much smaller space requirement for storage
- Simplicity of metering and automatic control
- Simplicity of operation and maintenance, since solution feed ammoniators are virtually identical to chlorinators
- Lower cost

## AQUEOUS AMMONIA ($NH_4OH$)

**Source and Availability.** While there may be a single source of ammonia locally there will be several distributors of ammonium hydroxide solution. The ammonia market is so competitive—domestic and foreign—that ammonia in either form is ubiquitous.

Local distributors have a fleet of trucks and will provide storage tanks upon request. Aqua ammonia costs about 14 percent more than anhydrous ammonia; however, storage tanks are less expensive than the pressurized tanks required for anhydrous ammonia.

Shipping can be made by 8000 gallon tank cars, 4000 gallon tank trucks, 375 and 750 gal. drums, or 30 gal. carboys.

**Physical and Chemical Characteristics.** Commercial strength is approximately 30 percent. The density of Grade A, 29.4 percent solution, is 0.8974 at 60°F compared to water at 1.

This strength solution corrodes copper, aluminum alloys, and galvanized surfaces. When this solution is dispersed into the process water by the diffuser a water softening reaction will occur at the perforation in the diffuser. This will promote the deposit of calcium scale in proportion to the hardness of the water. Provisions should be made to allow the diffusers to be cleaned with acid or chlorine solution.

**Potential Hazards.** Ammonium hydroxide is a caustic solution and can be hazardous to persons in contact with the solution. Usual precautions required for caustic solutions should be observed.

If the solution is being applied at an installation using hypochlorite solution, steps must be taken to prevent aqua ammonia solution from being unloaded into the hypochlorite storage tank or vice versa. In such an event an explosive mixture of nitrogen trichloride is likely to form with disastrous results. If not, the evolution of nitrogen trichloride is certain to cause a hazardous air pollution problem.

## SUPPLY SYSTEM

**Storage Tanks.** The local supplier should be consulted on this matter. Make certain the supplier incorporates all of the necessary piping to facilitate unloading and that the tank has a proper sight glass. Tank and appurtenances should be made of mild steel. The words "AQUA AMMONIA—$NH_4OH$ CAUSTIC" in large letters should be highly visible on each side of the tank.

## METERING AND CONTROL SYSTEM

**Design Considerations.** The most difficult part of the aqua ammonia facitity to design properly is the metering and control system. It is most exacting because ammonia N has to be applied at a constant ratio to chlorine. Depending upon local conditions this ratio will be approximately 4 to 1 chlorine to ammonia. This means the feed rates will be 3–5 times lower than chlorine. Furthermore, since the aqua ammonia will be about 30 percent $NH_3$ or 300,000 mg/l compared, to

10,000 mg/l anhydrous ammonia solution in a solution feed ammoniator, the designer is faced with the problem of precise control of small quantities of solution. For example, a water supply uses 50 lb/day chlorine and the ammonia-N requirement is 12.5 lb/day (4 : 1 ratio); then at 2.25 lb $NH_3$-N per gallon of 30 percent solution an aqua ammonia feed rate of only 0.23 gallons per hour will be required. Obviously aqua ammonia is not suitable for small water supplies unless it is diluted with softened water.

**Diaphragm Pumps.** These are widely used in waterworks practice when they fit the requirements. If these pumps can fit the metering requirement the control system should be patterned after those described in Chapter 2 for hypochlorite.

The designer should strive to eliminate pulsing activity of the diaphragm pumps in order to salvage the range and accuracy of flow metering equipment required to control these pumps.

**Diffusers and Solution Lines.** Reasonable care should be used in the design of the solution lines in order to minimize transit time and thereby decrease system dead time. This will make the system more compatible with the chlorinator control system.

Owing to the fact that there are no real back-pressure (up to 125 psi) problems when using diaphragm pumps, the designer is free to put the required head loss into the diffuser (8–12 ft) to provide good mixing with the process water.

All diffusers should be in duplicate so that they may be taken out of service for cleaning to remove scale deposits caused by hardness in the water.

## RELIABILITY PROVISIONS

This is not a factor in water treatment. Ammonia application interruptions for short periods will do little harm. THM formation may escalate during these periods. Health effects of such an event are unknown and are probably insignificant. Disappearance of ammonia in the treatment process may result in off-flavors at the consumer's tap. This may or may not result in consumer complaints.

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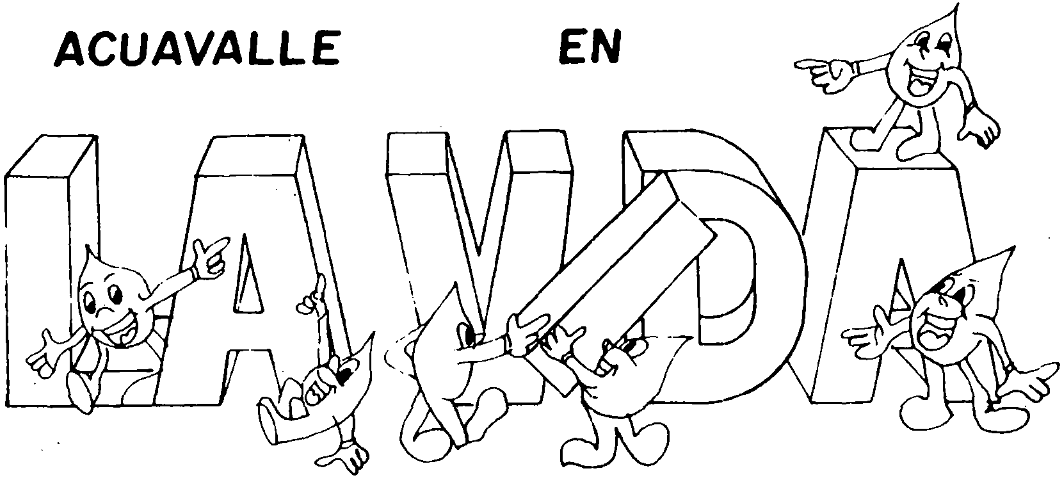

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