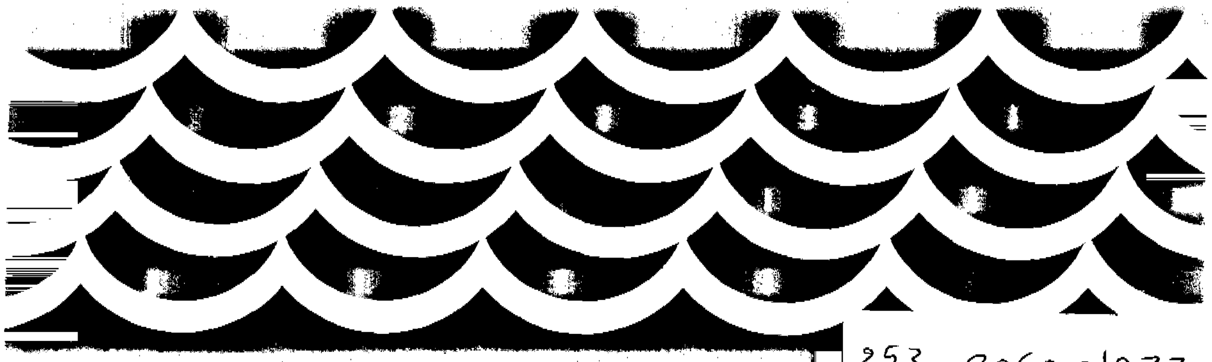
COAGULATION
and
FLOCCULATION

With an emphasis on water and wastewater treatment

by
JOHN BRATBY



"Coagulation and Flocculation"

Coagulation and flocculation play a dominant role in many water and wastewater schemes. Because of a complex interdependence of numerous factors inherent in the coagulation and flocculation processes, a thorough understanding of the phenomena involved is essential. To date, pertinent current literature does not present an overall account of coagulation and flocculation in a single publication; as a consequence, the reader lacks an overall picture of the processes as a whole and, without further extensive literature searching, succeeds in achieving only a superficial understanding. This new book has been written to fill the conspicuous gap in the current literature. The subject matter is presented logically and sequentially from theoretical principles to practical applications such that the reader gains an overall in-depth understanding of the processes as a whole.

The Author The form of presentation of the book is a reflection of the author's background. Dr. Bratby, author of numerous technical papers and articles, held the position of Senior Research Officer of the Water Research Commission of South Africa at the University of Cape Town and, at the present time is Contract Technical Consultant with CAESB, the Brazilian government organisation responsible for environmental protection, water and sewage treatment etc. in the Federal District of Brasilia.

In its present form the book evolved from material offered to undergraduate and postgraduate university students. Although it has been progressively modified and increased in scope so as to cater for the requirements of practising chemists, chemical and civil engineers involved with water and wastewater treatment, the book retains a didactic nature. Therefore, the book is designed to serve three purposes: (1) A readable and useful presentation for the water scientist and engineer; (2) A convenient reference handbook in the form of numerous examples and appended information and (3) Course material for under- and postgraduate students.

COAGULATION AND FLOCCULATION

JOHN BRATBY

WITH AN EMPHASIS ON WATER AND WASTEWATER TREATMENT

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TO JENNY

Ἀστέρας εἰσαθρεῖς ἀστὴρ ἐμός.

Εἴθε γενοίμην οὐρανός,

Ὡς πολλοῖς ὄμμασιν εἰς σὲ βλέπω.

PLATO (Greek Anthology. Bk. vii, epig. 669)

Preface

Coagulation and flocculation play a dominant rôle in many water and wastewater treatment schemes. Because of a complex interdependence of numerous factors inherent in the coagulation and flocculation processes, a thorough understanding of the phenomena involved is essential.

In general, pertinent current literature does not present an overall account of coagulation and flocculation in a single publication. Moreover, a given publication may emphasise theoretical aspects with little indication of the practical significance of the phenomena, or, largely ignores the theoretical development and presents essentially practical material only. In most cases, the uninitiated reader lacks an overall picture of the processes as a whole and, without further extensive literature searching succeeds in achieving only a superficial understanding.

This book has the intention of remedying the above inadequacies. An attempt has been made to present the subject matter logically and sequentially from theoretical principles to practical applications. Successive chapters deal with, in turn, properties of materials present in waters and wastewaters; characteristics and types of coagulants commonly in use, mechanisms and practical implications of destabilization of waterborne material using metal coagulants and polyelectrolytes respectively; considerations related to coagulant addition at the "rapid mixing" stage; theoretical and practical considerations of flocculation and details of experimental procedures for assessing primary coagulants, flocculant aids, sludge conditioners and flocculation parameters. Numerous examples are included as appropriate.

Disposal of sludges resulting from coagulation-flocculation related operations is dealt with in the Appendix. This important topic has been separated from the main text so as to avoid disturbing the continuum of the presentation. The Appendix also includes a "ready reference" information source of coagulation-flocculation applications. The objective in compiling information in this fashion is to provide an a priori *guide* to coagulant types, dosages and conditions of application; provisions for flocculation; related solid-liquid separation facilities and so on, for numerous applications.

The book in its present form evolved from material offered to undergraduate and postgraduate university students. Although it has been progressively modified and increased in scope so as to cater for the requirements of practicing chemists, chemical and civil engineers involved with water and wastewater treatment, the book still retains a didactic nature. Therefore, it is hoped that the book will serve three functions:

1. A readable and useful presentation for the water scientist and engineer ;
2. A convenient reference handbook in the form of numerous examples and appended information;
3. Course material for under- and postgraduate students.

I wish to express my appreciation of the following: Professor G.V.R. Marais, University of Cape Town, whose example as a research worker has always been an inspiration; The Water Research Commission of South Africa under the Chairmanship of Dr. G. J. Stander who, through their intelligent sponsorship, contributed to a healthy research atmosphere which I enjoyed at the University of Cape Town; Mr. Ian Reed, consultant engineer, Ninham Shand and Partners Inc., for many fruitful discussions and especially his help with parts of Chapter 6; Universidade de Brasília, in particular Professor Marco Antonio A. Souza of the Department of Civil Engineering, for authorization to use the University library facilities; Mr. Derek B. Purchas, consultant chemical engineer and

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PARTICLE SIZE mm	CLASSIFICATION	EXAMPLES	TOTAL SURFACE AREA m^2/cm^3	TIME REQUIRED TO SETTLE 100mm IF SP. GRAVITY=2.65
10	COARSE DISPERSION (visible to naked eye)	Gravel, coarse sand, fine sand, mineral substances, precipitated and flocculated particles, silt and macroplankton	6.10^{-4}	0.1 second
1			6.10^{-3}	1 second
0.1			6.10^{-2}	13 seconds
0.01	FINE PARTICULATE DISPERSION (visible under microscope)	Mineral substances, precipitated and flocculated particles, silt, bacteria, plankton and other organisms	0.6	11 minutes
0.001			6	20 hours
0.0001			60	80 days
0.00001	COLLOIDAL DISPERSION (submicroscopic)	Mineral substances, hydrolysis and precipitation products, macromolecules, biopolymers, viruses	600	2 years
0.000001			6000	20 years
$< 10^{-6}$ mm	SOLUTION	Inorganic simple and complex ions, molecules and polymeric species, polyelectrolytes, organic molecules, undissociated solutes, small aggregates		

TABLE 1.1 - CLASSIFICATION OF PARTICLE SIZES

gates of precipitated and flocculated matter, silt, bacteria, plankton, viruses, biopolymers and macromolecules. Material smaller than approximately 10^{-6}mm are referred to as comprising solutions. Such material includes inorganic simple and complex ions, molecules and polymeric species, polyelectrolytes, organic molecules, undissociated solutes, small aggregates and so on.

Particles of colloidal or lesser dimensions are able to retain a dispersed or dissolved state because of certain inherent characteristics which promote their *stability*. The term stability refers to the capacity of such particles to remain as independent entities within a dispersion.

All particles in a liquid medium possess certain properties associated with interfacial phenomena. Such phenomena (to be discussed in detail in Chapter 2) include the effects of the surface charge carried by particles and the degree of hydration (or solvation) of the particles' surface layers.

It is due to the overriding influence of surface phenomena that colloids, which possess a colossal surface area to mass ratio, have the ability to exist as stable dispersons: For illustrative purposes, Table 1.1 presents the total surface area for an original particle of diameter 10mm split into (reformed) spheres of progressively smaller diameters. It is seen that as the size of particles become progressively smaller, for a given total particle mass the total surface area becomes extremely large. Hence, it is apparent that for a given total mass, the smaller the particles the more predominant become the influence of phenomena associated with interfaces. Moreover, the lesser become the influence of gravity effects associated with mass.

With particulate material in the colloidal size range, it is apparent from Table 1.1 that, considering hydrodynamic effects alone, time scales of up to several years may be required for colloidal material to settle through a significant distance. Furthermore, because of a number of phenomena to which such small particles are subjected, a change in position arising from gravity effects could, in a statistical sense, involve geological time spans. Such phenomena, which include thermal convection currents within the dispersion medium, molecular and ionic bombardment and so on, serve to maintain particles in effectively permanent suspension.

It is feasible that colloidal particles may be removed from dispersions by methods other than those relying on gravity effects. Such methods include adsorption and physical straining. Figure 1.1(7) demonstrates various filter types and the size spectrum of dispersed material to which they may be applicable. In the engineering sense, considering the volumes involved in water and wastewater treatment, direct adsorption or straining by means of a given filter type is not economically feasible, although exceptions may exist in certain industrial processes.

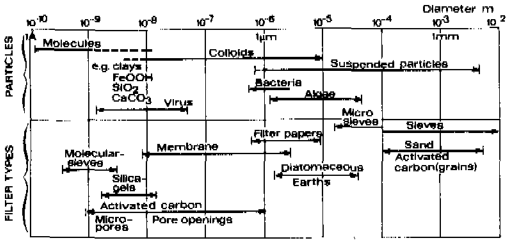

FIGURE 1.1: Size Spectrum of Waterborne Particles and Filter Pores. (After Stumm(7)).

From the preceeding comments, the meritoriousness of processes which convert fine particulate, colloidal or dissolved material into a form whereby separation from the dispersion or solvent is practicable, is self apparent. Such processes could either (i) alter the surface properties of particulate material thereby increasing the adsorptivity of the particles to a given filter medium or generating a tendency for aggregation of small particles into larger units or (ii) precipitate dissolved material thereby creating particulate material for which separation by sedimentation and/or filtration is feasible. Such a conversion of the stable state of a given dispersion or solution to an unstable state is termed destabilization.

The processes which are able to accomplish destabilization of waterborne particulate or dissolved material are coagulation and flocculation.

1.1 DEFINITIONS

Ideally, this section should commence with widely accepted definitions of coagulation and flocculation so as not to perpetrate confusion. However, when the abundant literature on the subject is consulted it becomes evident that a number of definitions have been variously adopted. Furthermore, it appears that at times the terms coagulation and flocculation have been used interchangeably, whichever definition has been accepted. It is apparent that a significant contribution to the existing confusion has been from the quarter of the water treatment industry, *which has for years used all manner of definitions of its own*(4).

There have been attempts(2) to remedy the lack of a universal set of definitions, but in certain respects there still remained a certain unsatisfactoriness. What is required is a lack of ambiguity and certainty in usage of terms during all possible conditions of chemical addition and configurations of the overall process. In this book the following definitions are adopted:

Coagulation is the process whereby destabilization of a given suspension or solution is effected. That is, the function of coagulation is to overcome those factors which promote the stability of a given system.

Flocculation is the process whereby destabilized particles, or particles formed as a result of destabilization, are induced to come together, make contact and thereby form large(r) agglomerates.

Primary coagulant refers to that chemical or substance added to a given suspension or solution to effect destabilization.

Flocculant aids are those chemicals or substances added to a destabilized suspension or solution to accelerate the rate of flocculation or to strengthen flocs formed during flocculation.

Sludge conditioners are those chemicals or substances added to a usually thickened suspension to promote dewatering and to strengthen flocs prior to dewatering processes.

Hence, for the case of a metal coagulant (for example aluminium sulphate, ferric chloride etc.) added to, say, a clay suspension, the metal coagulant is being employed as a primary coagulant. If a cationic polyelectrolyte were to be added in place of the metal coagulant then one would refer to the polyelectrolyte as the primary coagulant. In both cases, the primary coagulant is added to destabilize the clay dispersion (see Chapter 3 for a full discussion of the types and characteristics of metal coagulants and polyelectrolytes).

If, in the case of metal coagulant addition to the clay suspension, an anionic polyelectrolyte, say, was subsequently added, in this instance the polyelectrolyte would be employed as a flocculant aid. Note that from the instant that the primary coagulant is added, flocculation begins immediately as a result of molecular bombardment. This flocculation stage, as will be explained further in Chapter 7, is termed *perikinetic flocculation*. However, for appreciable floc formation, some form of induced turbulence in the suspending medium is required. This stage, termed *orthokinetic flocculation* is effected by mechanical agitation or by inducing a tortuous flow pattern to the suspending medium by passage through granular filter media or around baffles installed in a flocculation tank.

After coagulation (during which destabilization has occurred) and flocculation (during which flocs of required size and characteristics have formed) the destabilized - flocculated stream is passed to a solid-liquid separation facility where flocs are either separated by gravity or are filtered from the liquid. The accumulated material may then be further treated to facilitate ultimate disposal. Polyelectrolytes are often added at this stage to enhance the dewatering charactistics of the material. In this case one refers to the polyelectrolyte as a sludge conditioner.

1.2 PERFORMANCE CRITERIA

Although the areas of application of the combined coagulation and flocculation processes vary widely, including those in the industrial and municipal wastewater treatment fields, by far the most extensive application has been in the area of potable water treatment.

With few exceptions, surface waters require some form of treatment before distribution as a potable supply complying with health standards. Table 1.2(5) presents a summary of water quality standards from a number of sources. For a more detailed list reference should be made to the *International Standards for Drinking Water*(9) published by the World Health Organization. Over and above physical and chemical quality criteria such as those presented in Table 1.2, of further importance are the bacteriological and virological qualities.

When evaluating a potential potable water supply, a thorough analysis is usually carried out thereby identifying those parameters particularly requiring treatment. In general, the initial phase of the appropriate treatment study is to assess the degree of removal of the pertinent parameters by coagulation and flocculation. Here, a number of separate primary coagulant types, various combinations of coagulants, different flocculant aids and so on, will be added to the water under study through a range of imposed experimental conditions. The experimental procedure universally adopted for this phase of study is the jar test, which is described in detail in Chapter 8.

TABLE 1.2: WATER QUALITY STANDARDS FOR DOMESTIC POTABLE WATER (5)

SUBSTANCES	UNITS	INTERNATIONAL WHO[9]		EUROPEAN WHO	UNITED STATES[8]	SWEDEN[3]	FRANCE[6]	BULGARIA[1]	TANZANIA[5]
		ACCEPTABLE	ALLOWABLE						
TOXIC SUBSTANCES									
Lead	µg/l	-	50	100	50	20/50**	-	100	100
Arsenic	"		50	50	50	10/50**		50	50
Selenium	"	-	10	10	10	10/50**	-	50	50
Chromium	"	-	50	50	50	20	-	50	50
Cyanide	"	-	200	50	10	10/20**	-	10	200
Cadmium	"	-	10	10	10	10	-	50	50
Barium	"	-	1000	1000	1000	-	-	1000	1000
Mercury	"	-	-		-	1/5**	-	-	-
Silver	"	-	-	-	50	-	-	-	-
HUMAN HEALTH									
Fluoride	mg/l		1,5	0,7	0,8 -1,7	1,5	-	0,7-1,0	8,0
Nitrate	"	-	30	50/100**	45	30	44	30	(100)
GENERAL USE									
Colour	mg/l Pt-Co	5	50	-	15	10	-	15	50*
Turbidity	mg/l SiO_2	5	25	-	3	weak	-	30cm†	30*
pH		7,0-8,5	6,5-9,2	-	-	6,0-8,0	-	6,5-8,5	6,5-9,2*
Total dissolved matter	mg/l	500	1500		-	200	2000		2000*
Total hardness	mg/l $CaCO_3$	-	-	500	-	-	300	450	600*
Calcium	mg/l	75	200				-	150	-
Magnesium	"	50	150	125	-	-	125	50	-
Sulphate	"	200	400	250	250	25/250**	250	250	600*
Chloride	"	200	600	600	250	25/250**	250	250	800*
Iron	"	0,3	1	1	0,3	0,2	0,2	0,2	1,0*
Manganese	"	0,1	0,5	0,05	0,05	0,05	0,1	0,1	0,5*
Copper	"	1,0	1,5	0,05	1,0	0,05/1,0**	0,2	0,2	3,0*
Zinc	"	5,0	15,0	5,0	5,0	0,3/5,0**	3	3	15,0*
Phenolic substances as Phenol	µg/l	1,0	2	1	1	-		1	2

*Tentative Figures

**Lower value refers to permissible concentrations in water purified according to "normal" practice i.e coagulation, flocculation, and filtration. Higher value for waters much more extensively treated

†Transparency measured as thickness of water layer through which standard type can be read

The criteria for the viability and/or optimum conditions for coagulation and flocculation applied to a potential or existing water supply, depend on the water constituents. In the majority of cases several constituents are of concern and, essentially, analysis of the water after coagulation and flocculation will be based on the removal of each. However, there will often be a particular constituent that may be taken as representative and which will be used as the criterion of process efficiency, especially for the initial phases of the viability study of a potential supply, or during routine control of an existing supply. In many instances, such constituents comprise those giving rise to turbidity and/or colour in a given water.

Because of the widespread usage of turbidity and colour as indicators of water quality, these criteria will be discussed in some detail below. However, it should be noted that there is no intended implication that turbidity and colour are generally predominant in defining the acceptability of a given water for human consumption. Moreover, the convenience and relative celerity in measuring these criteria does not preclude the more laborious measurements involved with other physical, chemical or biological criteria.

1.2.1 Turbidity

Turbidity may be identified as the lack of clarity of a water. However, turbidity should not be confused with colour; it is very possible for a water to be dark in colour yet clear and not turbid. Suspended matter giving rise to turbidity include silt, bacteria, algae, viruses, macromolecules and material derived from organic soil matter, mineral substances, many industrial pollutants and so on. Hence, it is self apparent that removal of turbidity from water involves the removal of a wide variety of substances.

Turbidity is not a direct measurement of the amount of suspended material in a given water but rather an arbitrary optical measurement based on interference of light passing through the water. There are two bases of turbidity measurement: turbidimetry and nephelometry.

Turbidimetry involves comparing the transmission of light through a standard suspension to that through the water sample. Instruments employing this technique are based on the Jackson candle turbidimeter, which consists essentially of three parts: a calibrated glass tube, a holder and a candle. With the tube in place over the lighted candle, the water sample is gradually added until the outline of the candle flame is no longer discernible. The level of the suspension in the tube defines the turbidity.

In large part due to the subjectivity of turbidimetry measurements, there has been a gradual evolution to the widespread use of nephelometry. With this technique, a light beam is directed into the water sample at right angles to the direction of response of photoelectric cells within the instrument. Light is scattered by the particles of the suspension and converted to a galvanometric reading. The phenomenon of light scattering by a turbid suspension is known as the *Tyndall* effect, after the British physicist who studied it extensively. The degree of scattering (or the intensity of the Tyndall light) is related to standard turbidity units. One standard turbidity unit is normally taken as the turbidity resulting from a standard suspension of formazin (1,25 mg hydrazine sulphate $(NH_2)_2.H_2SO_4$ and 12,5 mg hexamethylenetetramine in 1 *l* turbidity free distilled water). Formazin polymer is currently used as the turbidity reference suspension because of its stability and reproducibility in turbidity measurements. Turbidities measured with formazin suspensions as standard are referred to as F.T.U. (formazin turbidity units).

Turbidity measurements are strongly influenced by the nature, size, concentration and refractive index of particles in suspension. Therefore, as a consequence there is no direct correlation between the amount of suspended material in a water sample and the turbidity of the sample.

Regarding the possible sources of turbidity given previously, the possibility of a human health hazard arising from toxicity, infection or gastrointestinal irritation is appreciated. Moreover, apart from the health point of view, turbidity is objectionable on aesthetic grounds: in other words, the potability of water less than a certain degree of clarity is considered to be doubtful by the general public. Furthermore, turbid supplies are unacceptable to many industrial consumers: for example, process water used in food and paper industries is required to have a high degree of clarity to assure adequate final product quality.

1.2.2 Colour

As will be discussed in greater detail in Section 4.2.2, most of the colour in waters arises from organic compounds leached from soil and decayed vegetation. Surface waters may at times appear to be highly *coloured*, because of coloured suspended matter, when in reality they are not. Colour caused by suspended matter is referred to as *apparent* colour and is differentiated from colour derived from organic sources, which is referred to as *true colour*.

Colour, like turbidity, is quantified in terms of arbitrary units since the concentration of colouring matter is not a measure of its colour producing properties. To measure the colour of a sample (see Section 4.2.2.4) the sample is compared to an arbitrary standard colour scale. The standard colour unit is defined as that colour produced by dissolving 1,0 mg potassium chloroplatinate and 0,5 mg cobaltous chloride in 1,0 litre of distilled water. The colour produced is of a yellowish-brown character and resembles that found in natural waters.

Coloured waters are objectionable for a number of reasons (see Section 4.2.2.3), not least of which include aesthetic considerations. Furthermore, the presence of colouring matter is an indication of pollution of some form and, therefore, steps are invariably taken to remove colour from waters during treatment. However, as far as humic colouring matter is concerned, there is no evidence of a health hazard.

1.3 SUMMARY

As a review of the preceeding discussions, one can put forward the following general comments: Coagulation is the process whereby a given system may be transformed from a stable to an unstable state. The manifestation of destabilization is dependent on the particular system: For example, in the case of disperse suspensions or solutions, visible floc or precipitate formation occurs; In the case of highly concentrated suspensions,dewatering of the *sludge mass* occurs, and so on.

Flocculation is the process whereby the manifestation of destabilization is realised in practicable terms: In effect, flocculation accelerates floc formation; influences the physical characteristics of flocs formed (for example, their strength, size and density) and governs the final number concentration of destabilized particles. Flocculation, by whatever means it is effected, is a necessary adjunct to destabilization.

Considering the wide variety of material of which coagulation and flocculation effect removal in the area of water treatment alone, one may say that these processes are veritable *work-horses* of whichever overall treatment scheme is applied. Such a diversity of material, ranging from clay particles through various biological forms to substances in solution, occur to differing extents simultaneously in a given water source and thereby present considerable difficulties during both optimisation and control of coagulation and flocculation. Optimisation is influenced by the properties of the material present, characteristics of the different coagulants which may be applied, method of addition of coagulants to the water and, with a particular combination of such factors, the characteristics of flocs formed for a given set of flocculation parameters: That is, the magnitude of induced velocity gradients, their duration and so on. Control is influenced largely by changes in water quality and, in cases where a range of materials are present, the relative concentration of each at a given time.

The complications inherent in coagulation and flocculation, outlined above, are most effectively overcome with the support of a thorough understanding of both the various phenomena involved and their interdependence. It is hoped that the following chapters contribute to the institution of such a level of apprehension.

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2

Colloids and Interfaces

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2.0 INTRODUCTION

In the introductory chapter of this book it was shown that the substances in water and wastewater treatment to which the coagulation-flocculation process is applied may generally be described as being within or less than the colloidal size range. Coagulation is the phase in the overall process whereby the constituents of a given water are destabilized and flocculation is the phase whereby destabilized particles, or *particles* formed during destabilization, are induced to collect into aggregates.

With colloids, the term *stability* describes the ability of individual particles to remain as separate entities or, in other words, to maintain a dispersed state. The stability of colloidal material arises from the predominance of forces associated with the solid-liquid interface. Principally, the interfacial forces promoting the stability of a colloidal dispersion arise from: (i) the presence of a surface charge at the interface between colloid and liquid and (ii) hydration of surface layers of the colloid, as shown conceptually in Figure 2.1.

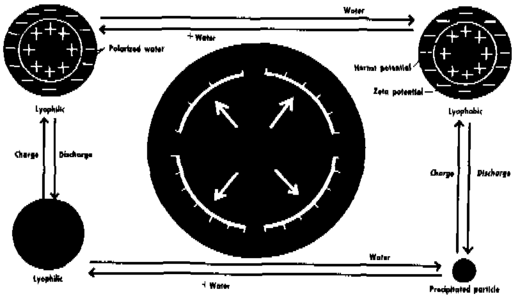


FIGURE 2.1: Stability of Colloidal Particles in Aqueous Suspension Depends on Hydration and Electrostatic Charge, Both of Which in Turn Depend on Chemical Composition and Structure of Substrate at the Solid-Liquid Interface. (From Priesing(28), with permission of the American Chemical Society).

There are two general classes of colloids, which are given the names lyophobic and lyophilic. In water and wastewater treatment the terms are made more specific with the names hydrophobic and hydrophilic. Hydro - refers to the water phase in which the colloids exist and - phobic and-philic refer to the *degree* of affinity of the colloids for the liquid phase. That is, hydrophobic infers water repellence and hydrophilic infers a strong affinity for water molecules in the surface layers of the colloid. The amount of water bound by hydrophilic particles may in some cases be three to ten times their own dry mass. Examples of hydrophobic colloids are gold sols, silver halogenides and nonhydrated metal oxides. Hydrophilic colloids include gelatin, starch, gums, proteins and all biocolloids, for example, viruses and bacteria.

In water and wastewater treatment, it is usually difficult to classify a particular water as being either a hydrophobic or hydrophilic colloid dispersion: Both types may co-exist in a particular system and, furthermore, there may be a continuous transition from one state to the other, as occurs for example, during treatment. A further difficulty in classification is that in some instances both hydrophobic and hydrophilic areas may exist on the colloids together.

Although the term hydrophobic infers a definite solid-water boundary, there is in reality a layer of water molecules, perhaps in some cases only a molecule thick, bound strongly enough to the colloid surface such that as the colloid moves in the water, the plane of shear is a water-water boundary: As shown in Figure 2.2 (adapted from Horne (17)), the water molecule exists as a dipole with a positive end resulting from the two bonded hydrogen atoms and a negative end from the two free pairs of electrons of the oxygen atom. The result of this charge distribution is a strong dipole moment of $1{,}84.10^{-18}$esu; In the conditions encountered in water and wastewater treatment, colloidal material almost always possesses a net negative surface charge. The effect of these two factors: the dipolarity of the water molecule and the surface charge carried by the colloid, is to (i) bind water molecules to the solid-liquid interface and (ii) orient water molecules, or alter the way in which molecules are arranged, in the vicinity of the charged surface. The influence of the charged surface on the molecular arrangement of water is reflected in the different dielectric constants of successive water layers with distance from the charged surface, as shown in Figure 2.3 (adapted from Bockris et al (9)).

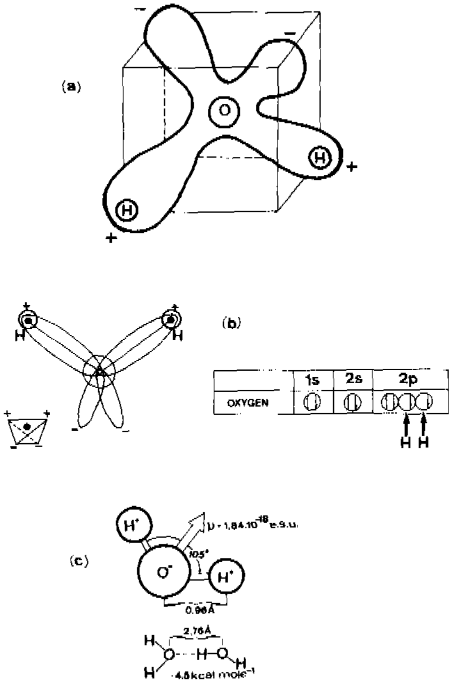


FIGURE 2.2: The Water Molecule: (a) Electronic Cloud; (b) Electronic Orbitals; (c) Structural Features and the Hydrogen Bond. (Adapted from Horne(17)).

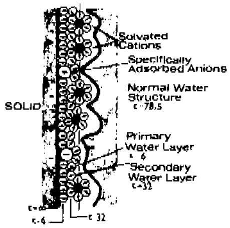


FIGURE 2.3: Position and Orientation of Water Molecules in the Electrical Double Layer. (Adapted from Bockris *et al*(9)).

The mechanism of destabilization of hydrophobic colloids is often considered as a reduction of the effective surface charge; reduction of the zone of influence of the surface charge and a reduction of the number of adsorbed water molecules or extent of zone of ordered water structure. The effect of these factors is that adjacent colloid particles, heretofore remaining apart principally due to electrostatic repulsion and to a certain extent to the ordered water structure around them, are now able to approach close enough together so that London-Van der Waal forces of attraction can hold them together. These latter forces are of an electrostatic character and arise from at least four components, of which by far the most dominant results from the interaction of two non-overlapping atoms: The electron cloud of each atom is attracted to the nucleus of the other with an intensity greater than the repulsions due to adjacent electron clouds and nuclei, such that the nett result is an *attractive* force of short range.

Although the above mechanism certainly does occur and may in some instances be dominant during destabilization, there are other phenomena of as great an importance, such as adsorption of polymeric ions or molecules. Here, although electrostatic considerations may play a rôle during destabilization, in certain cases the dominant mechanism may be one of *bridging* by the adsorbed polymeric species between adjacent particles. A further mechanism, of importance with removal of dissolved substances from water during coagulation, is the formation of precipitates. This mechanism is also probably of high significance during destabilization of hydrophilic colloid dispersions. Again, electrostatic considerations arising from the surface charge carried by the colloids may play a part during destabilization, but it is likely that the extensive hydration of surface layers of hydrophilic particles has the effect of a physical barrier. Destabilization is brought about principally by dehydration and coordinative chemical reactions between the applied coagulant and functional groups on the colloid surface.

From the above discussion, it is seen that destabilization reactions of colloids in aqueous dispersion are complex and arise from several mechanisms. The predominant mechanism depends very largely on two factors: (i) the nature of the colloidal dispersion: whether hydrophobic or hydrophilic particles are prevalent; the surface nature of the colloid, for example with hydrophilic particles, the types of functional groups present; the intensity of surface charge carried by the colloid and so on and (ii) the type of coagulant added to the colloid dispersion: whether coagulant species are uncharged or charged; the intensity of charge in the latter instance; the adsorptive capacity of the species; the capacity for bridge formation between adjacent colloids and so on.

For an understanding of destabilization phenomena of colloid dispersions with coagulant addition, the first steps are to consider the surface charge carried by hydrophobic colloids, the effect or zone of influence of the surface charge, the effect of simple coagulants on both the effective surface charge and its zone of influence, and destabilization of hydrophobic colloids with simple coagulants. These aspects are the subject of the present chapter.

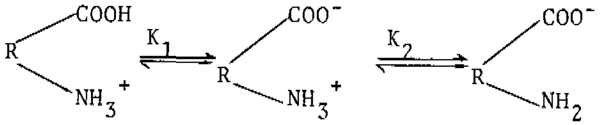
Subsequent chapters will deal with, in turn, more complex coagulants with enhanced adsorptive capacity and facility for bridge formation; the destabilization of hydrophobic colloids by such coagulants and destabilization of hydrophilic colloids and substances in solution.

2.1 ORIGIN OF SURFACE CHARGE

Before discussing what effect the surface charge of a colloid has on its environment, it is necessary to state the origin of this surface charge.

There are three principal ways in which the surface charge may originate(34):

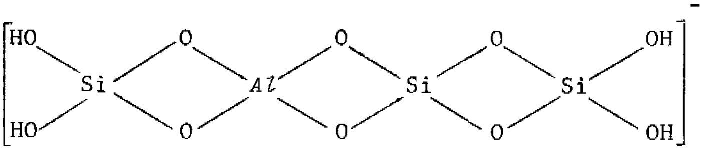
(i) The charge could arise from chemical reactions at the surface. Many solid surfaces contain functional groups which are readily ionizable, such as -OH; -COOH; $-OPO_3H_2$. For example, with a bacterium, the overall charge may be visualized as resulting from ionization of functional amino and carboxyl groups:



The charge of particles with such surfaces becomes dependent on the degree of ionization (proton transfer) and consequently on the pH of the surrounding liquid. At low pH values, a positively charged surface prevails while at higher pH, a negatively charged surface prevails. At some intermediate pH (the isoelectric point or the zero point of charge pH_{ZPC}), the charge will be zero.

Surface charges can also originate by processes in which solutes become co-ordinatively bound to solid surfaces.

(ii) Surface charge could be caused by lattice imperfections at the solid surface. For example, if in an array of solid SiO_2 tetrahedra a Si atom is replaced by an *Al* atom (*Al* having one electron less than Si), a negatively charged framework is established, viz:



Clays are examples of such atomic substitutions. Surface charges of this type are independent of the pH of the liquid.

(iii) Surface charges could also be established by the adsorption of ions. Adsorption of one type of ion on a surface can arise from London-van der Waal's forces and from hydrogen bonding.

2.2 EFFECT OF SURFACE CHARGE

The surface charge influences the distribution of nearby ions in the liquid. Ions of opposite charge (counter-ions) are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface. This, together with the 'mixing' tendency of thermal motion and mutual ionic repulsion or attraction, leads to the formation of an *electrical double layer* made up of the charged surface and a neutralizing *excess* of counter ions over co-ions distributed in a diffuse manner in the nearby liquid. The theory of the electrical double layer (see Sections 2.4, 2.5 and 2.6) deals with this distribution of ions and hence with the magnitude of the electric potentials which occur in the locality of the charged surface.

Electric potential is analogous to gravitational potential, but now one thinks of points in an electric field. Thus in the field around a negative charge, for example, another negative charge moves from points near the charge to points further away and one may say that points around the charge have an 'electric potential' whose magnitude depends on their relative proximity to the charge.

The electrical double layer can be regarded generally as consisting of two regions: an inner region which probably includes water molecules and adsorbed (hydrated) ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion.

Historically, the electrical double layer was first considered to consist of a charged surface and a diffused region of ions around that surface. This led to a model developed by Gouy and Chapman. The second development was to consider, in addition to the diffuse region of ions, a region in which ions are adsorbed and held to the surface. This led to the model developed by Stern. Stern's model therefore is a modification of the Gouy-Chapman model, with an adsorbed layer of ions being considered.

The development of the electrical double layer presented here will first deal with Stern's consideration of an adsorbed layer of ions, then the treatment for the diffuse part of the double layer (due to Gouy and Chapman) and finally Stern's model for the complete double layer.

2.3 ADSORPTION

Since the acknowledgement of adsorption is inherent in Stern's model of the electrical double layer, it is considered worthwhile to briefly consider what is meant by it. Adsorption of a molecule (or ion) from solution on the surface of a solid involves a sequence of events (34):

a) Removal of the molecule from solution;
b) Removal of solvent from the solid surface and
c) Attachment of the molecule to the surface of the solid.

Because of thermal agitation, molecules and ions in solution are in a continuous state of movement. As a consequence, colloidal particles are haphazardly bombarded by molecules giving rise to a random motion. This continuous random movement of colloidal particles is known as Brownian motion (after the British botanist Robert Brown who showed in 1827 that such motion was not confined to living matter, as originally supposed.) Because of Brownian motion there will frequently be collisions and contact made between molecules and ions in solution and solid surfaces. When such contact occurs, three events are possible:

(i) The molecule or ion could be held to the solid surface by ionic, covalent, hydrogen or dipolar bonding. These types of bonds may be classified in terms of bond energies (kcal mole^{-1}): ionic crystal bonds have a bond energy greater than 150; covalent between 50 to 100; hydrogen bonds 1 to 10 and polar less than 5. Adsorption arising from such mechanisms is referred to as chemical adsorption. Adsorption could also arise from (and is always enhanced by) London-van der Waal's forces of attraction. Adsorption arising from this mechanism is referred to as physical adsorption.

(ii) The molecule could be repelled from the surface by means of electrostatic repulsion before event (i) can take place.

(iii) Even if conditions are favourable for attachment, the molecule could once more be installed in solution because of natural Brownian movement.

The affinity of the solid surface for some solutes (those molecules, etc., in solution) may be less than the solid's affinity for the solvent itself (e.g. water molecules in the case of an aqueous solvent). Organic dipoles and large organic ions are preferentially accumulated at the solid surface primarily because their hydrocarbon parts have little affinity for water. Simple inorganic ions such as Na^+; Ca^{2+} and Cl^-may remain in solution, even if they are specifically attracted to the solid surface ; because they are readily hydrated in aqueous solutions. Less hydrated ions, such as Cs^+, $CuOH^+$ and many anions tend to seek positions at the solid surface to a larger extent than easily hydrated ions.

If adsorption does take place in solution, it follows that there is a net release of energy since the energy of attraction between the solid surface and the adsorbate must be greater than the energy of repulsion (if it is present) due to electrostatic effects. Furthermore, since adsorption involves the removal of a certain amount of solvent from the solid surface, then it follows that the energy required to remove the solvent molecules must be less than the energy released by the attachment of the adsorbate (See Figure 2.4).

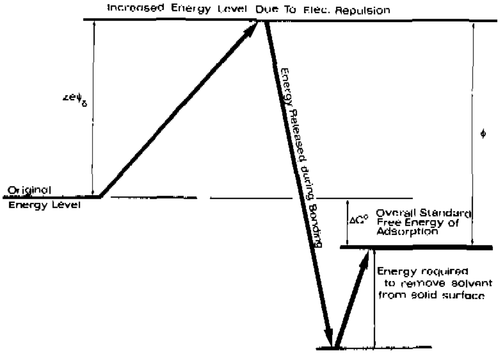


FIGURE 2.4: Scheme of Energy Changes During Adsorption

This energy released as a consequence of adsorption is termed the 'overall standard free energy of adsorption' and is given the symbol $\Delta\bar{G}^o$. From the discussion above it follows that $\Delta\bar{G}^o$ is equal to the sum of the energy released by the 'satisfaction' of whatever forces of attraction prevail (chemical bonding, London-van der Waal's forces, etc.) and either the energy released by the 'satisfaction' of electrostatic forces of attraction <u>or</u> the energy which has to be overcome because of electrostatic forces of repulsion.

Hence $\Delta\bar{G}^o$ is given by:

$$\Delta\bar{G}^o = \phi \pm ze\psi_\delta \qquad (2.1)$$

Where ϕ is the energy released during 'bonding' and $ze\psi_\delta$ is the energy *either* released or adsorbed during electrostatic interactions (see later). If $ze\psi_\delta$ is of opposite sign to ϕ yet is smaller in magnitude, then adsorption takes place quite readily.

Experimentally it is difficult to separate the energy of adsorption into its chemical and electrostatic components, but it is known that many organic ions of similar charge to the surface are readily adsorbed, indicating that the chemical adsorption energy released can easily be greater than the electrostatic energy of repulsion. Stumm and O'Melia (35) present a numerical example illustrating the above points:

For the adsorption of a monovalent organic ion to a surface of similar charge and against a potential drop (ψ_δ) of 100mV, the electrostatic term in Eq. (2.1), $ze\psi_\delta$=2,3 kcal mole^{-1}. The standard chemical adsorption energy for typical monovalent organic ions is of the order -2 to -8 kcal mole^{-1}, which demonstrates that the electrostatic contribution to adsorption can easily be less than the chemical contribution. From this, it is at least qualitatively appreciated that the addition of suitable counter ions not only decreases the effective surface charge, but may produce a reversal of surface charge at higher concentrations.

The adsorptivity of a particular system is described by empirical expressions, known as isotherms, which relate the mass of solute adsorbed per unit mass of adsorbent to the concentration of solute remaining after adsorption. Two widely used isotherms are the Langmuir and Freundlich isotherms.

For systems exhibiting Langmuirian adsorption behaviour, the relevant parameters fit the equation:

$$C/(x/m) = a + C/b \qquad (2.2)$$

Where C = concentration of solute (those molecules and ions in solution) which remains after adsorption (mgl^{-1});

x/m = mass of solute adsorbed per unit mass of adsorbent;

a, b = constants for a particular system.

Systems of interest here which exhibit Langmuirian adsorption behaviour are the destabilization characteristics often observed with hydrolyzed iron (FeIII) coagulants (35) and with polyelectrolytes (5,10). For the latter case, a modified Langmuir type isotherm, known as the Simha-Frisch-Eirich (S.F.E.) isotherm, has been used to describe polyelectrolyte adsorption behaviour (See Section 5.1.2.2). However, in many cases the Langmuir isotherm has been found to provide adequate representation of the phenomena.

For systems exhibiting Freundlichian adsorption behaviour, the appropriate equation is as follows:

$$\mathrm{Log}(x/m) = (1/a)\log C + \log b \qquad (2.3)$$

Freundlich adsorption behaviour has been reported(7) for the destabilization characteristics of dilute clay suspensions by hydrolyzed aluminium sulphate. The difference between the adsorption behaviour of aluminium coagulants compared to ferric coagulants and polyelectrolytes serve as a further indication of the complexity of the aluminium hydrolysis products formed (see Section 3.1.2.4).

2.4 INNER PART OF ELECTRICAL DOUBLE LAYER

The treatment of the diffuse part of the double layer proposed by Gouy and Chapman (see later) is based on an assumption of point charges in the electrolyte solution. However, Stern recognized that the finite size of the ions will limit the inner boundary of the diffuse part of the double layer since the centre of an ion can only approach the surface to within its (hydrated) radius without becoming specifically adsorbed. Stern proposed a model in which the double layer is divided into two parts separated by a plane (the Stern plane) located at about a hydrated ion radius from the surface (See Figures 2.5 and 2.6). The adsorbed ions may be dehydrated in the direction of the solid surface so their centres will lie somewhere between the solid surface and the Stern plane. Ions whose centres are located beyond the Stern plane are considered to be part of the diffuse layer for which the Gouy-Chapman treatment (see next section) is considered applicable. The electric potential at the surface of the particle is given by ψ_0 (or the Nernst potential) and that of the Stern plane (the Stern potential) is given by ψ_δ. The potential in the diffuse layer decays exponentially from ψ_δ at the Stern plane to zero at infinity (see later).

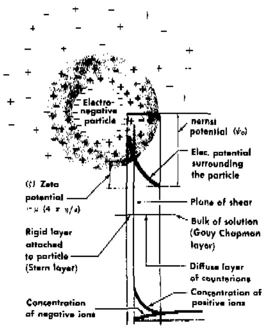


FIGURE 2.5: Conceptual Presentation of the Electrical Double Layer. (From Priesing$^{(28)}$, with permission of the American Chemical Society).

When specific adsorption takes place (i.e. adsorption arising from electrostatic and/or van der Waal forces) counter-ion adsorption generally predominates over co-ion adsorption and such a situation is depicted in Figure 2.6

It is possible, especially with polyvalent or surface active counter ions for reversal of charge to take place within the Stern layer, i.e. for ψ_0 and ψ_δ to have opposite signs (See Figure 2.7).

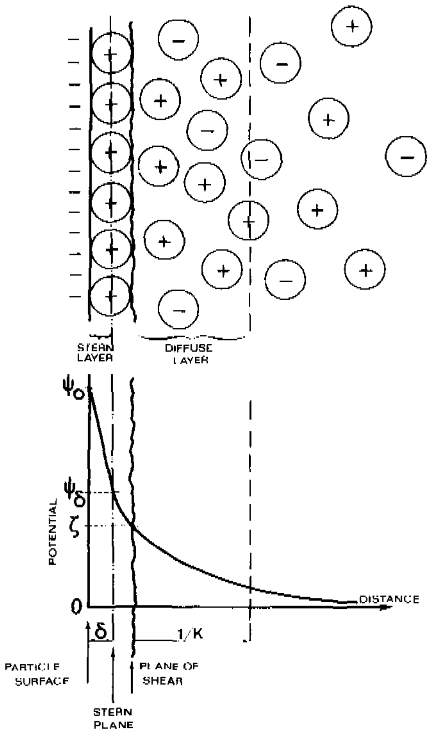


FIGURE 2.6: Counter-Ion Adsorption Generally Predominates Over Co-Ion Adsorption

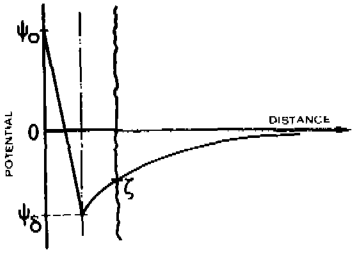


FIGURE 2.7: With Polyvalent or Surface-Active Counter-Ions, Reversal of Charge May Take Place Within the Stern Layer.

Adsorption of surface active co-ions could create a situation in which ψ_δ has the same sign as ψ_o and is greater in magnitude (See Figure 2.8).

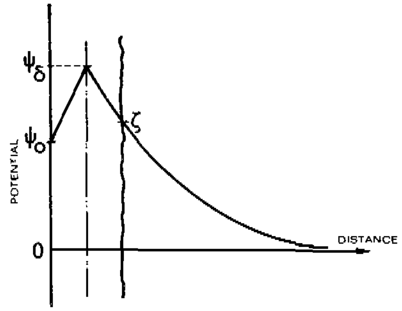


FIGURE 2.8: Adsorption of Surface-Active Co-Ions Could Increase Effective Surface Charge

2.5 DIFFUSE PART OF ELECTRICAL DOUBLE LAYER

2.5.1 Assumptions

The Gouy-Chapman treatment for the diffuse part of the double layer is based on the following assumptions[30]:

1. The surface is assumed to be flat, of infinite extent and uniformly charged.

2. The ions in the diffuse part of the double layer are assumed to be point charges distributed according to the Maxwell-Boltzmann distribution. This distribution is based on probability theory and leads to an expression for the number of molecules (ions) in a gas (liquid) at equilibrium possessing a certain specified energy. It considers a system made up of n_o similar molecules which do not attract or repel each other. The original expression for the distribution was:

$$n_i = n_o \exp\left(- \frac{E_i}{kT} \right) \tag{2.4}$$

where n_i is the number of molecules with energy E_i at absolute temperature, T. kT is Boltzmann's constant times absolute temperature and is a measure of the thermal kinetic energy of the particles. It is derived from entropy and probability considerations where the entropy of a system S is related to the probability of that system, W, by the equation:

$$S = k \log_e W$$

or

$$W = \exp\left(\frac{S}{k}\right) \tag{2.5}$$

W was defined by Boltzmann to be the ratio of the probability of an actual state to one, having the same total energy and volume, in which the molecules are completely ordered.

3. The liquid is assumed to influence the double layer only through its permittivity, which is assumed to have the same value throughout the diffuse part of the double layer. The permittivity may be conceptually visualized by considering it to be the inverse of the resistance to electron flow, that is, the lower the permittivity, the greater is the resistance to flow experienced by electrons.

2.5.2 Distribution of Potential with Distance from Charged Surface.

Let the electric potential at the Stern plane be ψ_δ and ψ at a distance x in the solution from the Stern plane.

Taking the solid surface to be negatively charged and that even with counter-ion adsorption, charge reversal has not taken place (which is the usual case) and an excess of counter-ions over co-ions exists in the diffuse layer, applying the Maxwell-Boltzmann distribution:

$$n_+ = n_o \exp\left(\frac{ze\psi}{kT}\right) \tag{2.6}$$

and

$$n_- = n_o \exp\left(-\frac{ze\psi}{kT}\right) \tag{2.7}$$

where n_+ and n_- are the respective numbers of positive and negative ions per unit volume at points where the potential is ψ, and n_o is the concentration of ions at infinity, i.e. at $\infty, n_+ = n_- = n_o$ (See Figure 2.5).

z = valency of ion
e = charge of electron
(hence ze = charge of ion)

The potential ψ at a point in an electric field - or in the diffuse layer - is defined to be the work done in moving a unit charge (of the same sign as that of the surface) from infinity to that point. If a charge of ze is moved from infinity to that point it follows that the amount of work done on it is $ze\psi$. That is, the charge is capable of performing $ze\psi$ units of work, which is the potential energy possessed by the charge at that point.

The charge density, ρ, at points where the potential is ψ is given by:

$$\rho = ze(n_+ - n_-)$$

$$= ze\ n_o \{\exp(\frac{ze\psi}{kT}) - \exp(-\frac{ze\psi}{kT})\}$$

$$\therefore\ \rho = +2ze\ n_o \sinh(\frac{ze\psi}{kT}) \qquad (2.8)$$

where $\sinh x = (e^x - e^{-x})/2$

ρ is related to ψ by Poisson's equation and for a <u>flat</u> double layer takes the form

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon} \qquad (2.9)$$

where ε= permittivity.

(Poisson's equation, derived from vector analysis, is based on Coulomb's law).

From equations (2.8)and (2.9):

$$\frac{d^2\psi}{dx^2} = -2\ \frac{zen_o}{\varepsilon} \sinh(\frac{ze\psi}{kT}) \qquad (2.10)$$

The boundary conditions for the latter equation are:

when $x = 0 : \psi = \psi_\delta$

when $x = \infty : \psi = 0$ and $\frac{d\psi}{dx} = 0$

The solution to the above equation is:

$$\psi = \frac{2kT}{ze} \ell n\{\frac{1 + \gamma \exp(-Kx)}{1 - \gamma \exp(-Kx)}\} \qquad (2.11)$$

$$\text{where } \gamma = \frac{\exp(ze\psi_\delta/2kT)-1}{\exp(ze\psi_\delta/2kT)+1} \qquad (2.11a)$$

$$\text{and } K = (\frac{2z^2e^2n_o}{\varepsilon kT})^{1/2} \qquad (2.11b)$$

At low potentials where $\psi << 25$ mV (and $\frac{ze\psi}{2kT} << 1$) one may use the approximation that $\exp(x) = 1 + x$

i.e. $\exp(\frac{ze\psi}{2kT}) = 1 + \frac{ze\psi}{2kT}$

Equation (2.11) thus simplifies to:

$$\psi = \psi_\delta \exp(-Kx) \qquad (2.12)$$

Equation (2.12) shows that at low potentials, the potential decreases exponentially with distance from the Stern plane. Close to the charged surface where the potential is likely to be relatively high, the above approximation cannot be used and the potential increases at a rate greater than exponential.

2.5.3 *Thickness* of Double Layer

The Stern potential ψ_δ can be related to the nett space charge density σ in the diffuse part of the double layer as follows:

$$\sigma = \int_0^\infty \rho dx$$

Substituting equation (2.8):

$$\sigma = \int_o^\infty 2ze\ n_o \sinh\frac{ze\psi}{kT}dx$$

$$= \int_o^\infty 2zen_o 1/2\ \{\exp(\frac{ze\psi}{kT})\ -\exp(-\ \frac{ze\psi}{kT})\}\ dx$$

$$= zen_o \int_o^\infty \{\exp(\frac{ze\psi}{kT})\ -\exp(\frac{ze\psi}{kT})\}\ dx \qquad (2.13)$$

At low potentials, again using the approximation that

$$\exp(\frac{ze\psi}{kT}) = 1 + \frac{ze\psi}{kT}$$

$$\therefore\ \sigma = zen_o \int_o^\infty \{(1 + \frac{ze\psi}{kT}) - (1 - \frac{ze\psi}{kT})\}dx$$

$$= \frac{2z^2e^2n_o}{kT} \int_o^\infty \psi dx \qquad (2.14)$$

But from equation (2.12):

$$\psi = \psi_\delta \exp(-Kx)$$

$$\therefore\ \sigma = \frac{2z^2e^2n_o\psi_\delta}{kT} \int_o^\infty \exp(-Kx)dx$$

$$= \frac{2z^2e^2n_o\psi_\delta}{kT}\ \{-\ \frac{\exp(-Kx)}{K}\}_o^\infty$$

$$= \frac{-2z^2e^2n_o\psi_\delta}{K\ kT}\ \{1/e^\infty - 1/e^0\}$$

$$= \frac{2z^2e^2n_o\psi_\delta}{K\ kT} \qquad (2.15)$$

But from equation (2.11b):

$$K = (\frac{2z^2e^2n_o}{\varepsilon kT})^{1/2}$$

$$\therefore\ \frac{2z^2e^2n_o}{kT} = \varepsilon K^2$$

Hence $\sigma = K\varepsilon\psi_\delta$

or, $\psi_\delta = \sigma/K\varepsilon$ (2.16)

From equation (2.16), the surface potential ψ_δ (at low potentials) is dependent on the nett space charge density σ; the permittivity of the diffuse layer ε and a quantity 1/K whose units are those of length e.g. cm. The significance of the quantity 1/K is demonstrated as follows:

Consider a parallel plate condenser whose plates are of *unit area* and separated by a distance d. The potential difference between the plates is V and the space between the plates is of permittivity ε, as shown in Figure 2.9.

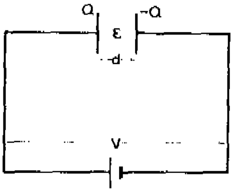


FIGURE 2.9: Parallel Plate Condensor Analogy With Electrical Double Layer.

The capacitance of the condenser is defined to be the ratio of the charge on either plate to the potential difference V between them,

i.e. $C = Q/V$

The permittivity is defined as:

$$\varepsilon = \frac{\text{Electric flux density}}{\text{Electric force}} = \frac{Q/1}{V/d}$$

$$= \frac{Q}{V}\frac{d}{1} = C\frac{d}{1} = Cd \text{ (for plates of unit area)}$$

Hence $C = \varepsilon/d$ for a parallel plate condenser (2.17)

Consider the diffuse part of the double layer where the potential differs from ψ_δ at the surface to zero at infinity.

The capacitance per unit area of the diffuse layer can be written as:

$$C = \frac{'Q'}{V} = \frac{\sigma, 1}{\psi_\delta - 0} = \frac{\sigma}{\psi\delta}$$

From equation (2.16) one can see that

$$\frac{\sigma}{\psi_\delta} \text{ (= capacitance) } = K\varepsilon \qquad (2.18)$$

For the parallel plate condenser it was shown that the capacitance between plates separated by distance d is equal to ε/d, hence, the diffuse layer may be considered to be a parallel plate condenser whose plates are separated by a distance of 1/K. For this reason 1/K is referred to as the *thickness* of the diffuse layer (or, alternatively, as the Debye-Hückel length). In reality, however, the diffuse layer extends to infinity.

2.5.4 Effect of Ionic Strength on Double Layer

As shown below, the thickness of the double layer is dependent on the ionic strength of the electrolyte solution. From Equation (2.11b):

$$K = \left(\frac{2z^2e^2n_o}{\varepsilon kT}\right)^{1/2} = \left(\frac{2z^2e^2}{\varepsilon kT}\,\frac{NCo}{10^3}\right)^{1/2} \qquad (2.19)$$

Where N = Avogadro's number = *number of ions* per mole of electrolyte solution = $6{,}03.10^{23}$ mole^{-1}.

C_o = concentration of electrolyte solution (moles ℓ^{-1}).

Rewriting Equation (2.11b) and putting $C_oz^2 = 2I$

where I = ionic strength (moles ℓ^{-1}).

$$K = \left(\frac{4e^2NI}{\varepsilon kT.10^3}\right)^{1/2} \qquad (2.20)$$

From Equation (2.20) it is seen that increasing the ionic strength results in a decrease in double layer thickness.

It can be calculated that for water at 20°C and ionic strength I, the thickness of the diffuse layer is given by:

$$K^{-1} = 2{,}0.10^{-8} \quad I^{-1/2}\text{cm} \qquad (2.21)$$

where

e = charge of electron = $1{,}6.10^{-19}$ coulombs

ε = permittivity = $7{,}08.10^{-12}$ coulombs $V^{-1}cm^{-1}$

kT = Boltzmann constant times absolute temp. = $0{,}41 \times 10^{-20}$V coulombs at 20°C.

2.5.5 Effect of Nature of Counter Ions

The Gouy-Chapman model also shows that multivalent counter ions are concentrated in the double layer to a much greater extent than monovalent ions, that is, from equation (2.6):

$$n_+ = n_o \exp(\frac{ze\psi}{kT})$$

it can be seen that for monovalent ions the expression can be written as

$$n_+ = n_o A$$

For divalent ions: $n_+ = n_o A^2$

For trivalent ions: $n_+ = n_o A^3$, etc.

2.6 STERN'S MODEL OF COMPLETE DOUBLE LAYER

Stern's complete model for the electrical double layer is based on considerations of electrical neutrality for the whole system.

If σ_o is the charge density at the particle surface, then treating the Stern layer as a condenser of thickness δ and with permittivity ε':

$$\sigma_o = \frac{\varepsilon'}{\delta}(\psi_o - \psi_\delta) \qquad (2.22)$$

Stern assumed that a Langmuir-type adsorption isotherm could be used to describe the equilibrium between ions adsorbed in the Stern layer and those in the diffuse part of the double layer. Considering only the adsorption of counter-ions, the charge density of the Stern layer is given by the expression:

$$\sigma_\delta = \frac{\sigma_m}{1+N/(n_o V_m)\exp\{(ze\Psi_\delta+\phi)/kT\}} \qquad (2.23)$$

where σ_δ	is the charge density of the Stern Layer;
σ_m	is the charge density of the Stern layer corresponding to a complete monolayer of counter-ions;
N	is Avogadro's number;
V_m	is the molar volume of the solvent;
ϕ	is the energy (per mole) of adsorption due to chemical forces; and
$ze\Psi_\delta$	is the energy (per mole) of adsorption due to electrostatic forces.

If σ is the charge density of the diffuse part of the double layer, then:

$\sigma = K\epsilon\Psi_\delta$ (See equation 2.16)

For overall electrical neutrality throughout the double layer, then

$\sigma_o + \sigma_\delta + \sigma = 0$

i.e.

$$\frac{\epsilon'}{\delta}(\Psi_o - \Psi_\delta) + \frac{\sigma_m}{1+N/(n_o V_m)\exp\{(ze\Psi_\delta+\phi)/kT\}} + K\epsilon\Psi_\delta = 0 \qquad (2.24)$$

Equation (2.24) is the Stern model for the double layer. It contains a number of unknown quantities of which the most significant is the Stern potential Ψ_δ. However, although ψ_δ cannot be directly measured, a close approximation may be obtained by determining the potential at the plane of shear, designated the zeta (ζ) potential, by electrokinetic measurements. This is the subject of Section 2.8.

2.7 COLLOID STABILITY IN TERMS OF THE DOUBLE LAYER

2.7.1 Energy of Interaction Between Particles

Verwey & Overbeek and Derjaguin & Landau independently developed a quantitative theory based on the Gouy-Chapman model in which the stability of hydrophobic colloids is treated in terms of the energy changes which take place when particles approach one another. The theory (known as the VODL theory) involves estimations of the energy of attraction (London-van der Waal's forces) and the energy of repulsion (overlapping of electrical double layers) in terms of the distance between particles.

The general expression developed for the repulsive energy V_R is very complex. However, for the condition of low ψ_δ and low values of exp (-KH), a relatively simple expression was developed by Verwey & Overbeek$^{(41)}$ which gives a good approximation for V_R:

$$V_R = \frac{B\varepsilon k^2T^2a\gamma^2}{z^2} \exp\ (-KH) \qquad (2.25)$$

where B is a constant equal to $4{,}36 \times 10^{20}\ A^{-2}\ S^{-2}$

A is Hamaker's constant (depends on the number of atoms per unit volume and the polarisability of the material of the particles).

$S = R/a = \dfrac{\text{distance between centres of spheres}}{\text{radius of spheres}}$

ε = permittivity = $7{,}08 \times 10^{-12}$ coulombs V^{-1} cm^{-1}

kT = Boltzmann constant times absolute temp. = $= 0{,}41 \times 10^{-20}$ V coulombs at 20°C

$\gamma = \dfrac{\exp\{ze\psi_\delta/2kT\}-1}{\exp\{ze\psi_\delta/2kT\}+1}$

H = shortest distance between spheres

z = valency of counter-ions

1/K = thickness of diffuse part of double layer.

The London-van der Waal's attraction energy between two molecules is of very short range and is assumed to vary inversely with the sixth power of the inter-molecular distance(14, 15, 16, 25). For an assembly of molecules, these forces are approximately additive and the attractive energy between two particles can be computed by summing the attractions between all pairs of molecules within the particles(25).

For the case of two identical spheres of radius a with the shortest distance between them equal to H (and H << a) then the London-van der Waal energy of attraction is approximated by(25):

$$V_A = \frac{-Aa}{12H} \tag{2.26}$$

There are certain difficulties involved in computing V_A, the main difficulty being the measurement of the Hamaker constant A.

The total energy of interaction between two charged particles is obtained by summation of the attraction and repulsive energies as shown in Figure 2.10.

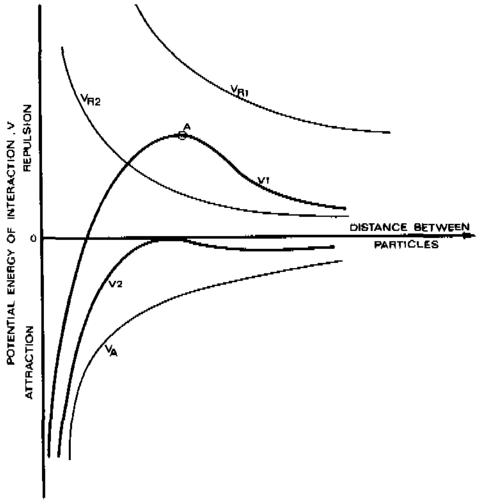


FIGURE 2.10: Potential Energy of Interaction Between Two Particles.

The general characteristics of the resulting potential energy-distance curve can be deduced from the properties of the two forces. The repulsion energy is an exponential function of the distance between the particles with a range of the order of the thickness of the electrical double layer (1/K). The attraction energy decreases as an inverse power of the distance between the particles. Consequently London-van der Waal's attraction will predominate at 'small' distances, (at *very* small distances there will be repulsion due to overlapping of electron clouds, known as the 'Born' repulsion - this is not shown on the potential energy curve). At intermediate distances double layer repulsion may predominate, depending on the relative values of V_A and V_R.

If the potential energy maximum (point A on Figure 2.10) is large compared with the thermal 'kinetic' energy of the particles(kT), the system will be stable. If the kinetic energy of the particles is large enough to surmount the potential energy 'hump', then the particles will coalesce. The height of this energy barrier depends upon the magnitude of ψ_δ and upon the range of the repulsive forces (i.e. upon 1/K).

2.7.2 Theoretical Optimal Concentration of Electrolyte for Destabilization.

An expression for the concentration of an indifferent electrolyte required to destabilize the dispersion can be derived by assuming that a potential energy curve such as V(2) in Figure 2.10 can be taken to represent the conditions for optimum destabilization:

From the curve there is a certain value of H at which V = 0 and $\frac{dV}{dH} = 0$.

Now,

$$V = V_R + V_A = \frac{B\varepsilon k^2 T^2 a \gamma^2}{z^2} \exp\{-KH\} - \frac{Aa}{12H} = 0$$

and

$$\frac{dV}{dH} = \frac{dV_R}{dH} + \frac{dV_A}{dH} = -KV_R - \frac{V_A}{H} = 0$$

i.e.

$$KHV_R + V_A = 0$$

But

$$V_R + V_A = 0$$

$$\therefore \quad KH = 1$$

Hence

$$\frac{B\varepsilon k^2T^2a\gamma^2}{z^2}\exp\{-1\} - \frac{AaK}{12} = 0$$

giving

$$K = 4{,}415\ \frac{B\varepsilon k^2T^2\gamma^2}{Az^2}$$

Substituting the expression found before for K, i.e. from Eq. (2.19):

$$K = \left(\frac{2e^2z^2N}{\varepsilon kT\ 10^3}C_o\right)^{1/2}$$

one can deduce that C_o, the molar concentration of electrolyte solution required to destabilize a colloidal dispersion, is given by:

$$C_o = \frac{9{,}75B^2\varepsilon^3k^5T^5\gamma^4 10^3}{A^2e^2Nz^6} \qquad (2.27)$$

2.7.3 Schulze - Hardy Rule

From Equation (2.27), an interesting point comes to light: Optimum concentrations of *indifferent* electrolytes yielding counter-ions with valency z = 1, 2, 3, etc., should be in the ratio $1/1^6 : 1/2^6 : 1/3^6$ or approximately 800 : 12 : 1. This is in reasonable agreement with experimental evidence on the coagulation of hydrophobic colloids by non-adsorbable ions. The phenomenon is known as the rule of H. J. Schulze and W. B. Hardy from their work in 1883 and 1900 respectively.

It should be noted that the above expression for the optimal concentration of indifferent electrolyte relies on a model for double layer depression according to the Gouy-Chapman treatment. It does not take into account the extensive adsorption likely during most instances of colloid destabilization with metal coagulants. For this reason, and because of the simplifications required in developing equations (2.25) to (2.27), the $1/z^6$ rule is inapplicable in most cases(21). However, there are instances where the Schulze-Hardy rule is observed. Such cases would include those where highly charged polynuclear coagulant hydrolysis species are present at low concentrations in solution (see Chapter 3). At sufficiently low concentrations adsorption may be negligible and the destabilization mechanism is one of double layer depression analogous to that of non-adsorbable ions. At higher coagulant concentrations adsorption concomitantly increases and the Schulze-Hardy rule becomes inapplicable(21).

2.8 ELECTROKINETIC MEASUREMENTS

2.8.1 Zeta Potential

It was stated in Section 2.6 that a difficulty in quantifying a model of the electrical double layer is measurement of the Stern potential ψ_δ. However, an approximation may be obtained by measuring the potential at the plane of shear between moving particle and surrounding liquid. This potential is known as the zeta (ζ) potential. The exact location of the shear plane is not known since it depends on the adsorbed ions in the Stern layer and the degree of hydration. It is assumed that the shear plane is located at a small distance further out from the surface than the Stern plane and that ζ is, in general, marginally smaller in magnitude than ψ_δ.

Zeta potential measurements are useful, not only in the testing of double layer theories (particularly in relation to the stability of lyophobic sols) but also in the following applications: (a) Colloid stability: This involves calculation of ζ potential and identification of ζ with the Stern potential ψ_δ; (b) Ion adsorption studies and (c) Characterization of particle surfaces: Studies of the effects of pH, surface active agents, enzymes etc. on zeta potential, give valuable information regarding the nature of particle surfaces. This technique has proved useful in characterizing the surfaces of bacterial cells etc.

The usefulness of zeta potential measurements in control of the coagulation-flocculation process is largely dependent on whether the destabilization mechanism is predominantly due to charge effects - in which case control to a given zeta potential may be feasible. However, in many cases charge effects are not the predominant mechanism, although they may play a rôle during destabilization. Therefore, in such instances, not only would adjustment to a given value of zeta potential (for example, zero) not necessarily lead to destabilization(23, 26, 35) but destabilization may not be predicted by any particular value of zeta potential. For example, Black _et al_(3, 6) found that with three separate types of clay turbid water using aluminium sulphate as coagulant, no reliable indication of the optimum conditions for destabilization could be inferred from zeta potential measurements (or more exactly, electrophoretic mobilities - see later). However, some workers(12) presenting results of zeta potential measurements have inferred that optimum conditions of coagulant type, dosage and pH etc. occur at the isoelectric point, i.e. at zero zeta potential, although no correlation with, say, jar test results is demonstrated. This is clearly misleading since it considers the destabilization mechanism to be solely that of charge neutralization which, as discussed earlier and as will be expanded in later chapters of this book, is a gross simplification in many cases.

In some cases, although charge neutralization may not be a pre requisite for destabilization, one may use the occurrence of surface charge response as a means of controlling the performance of certain processes relying on destabilization. For example, control of cationic polyelectrolyte dosage prior to a direct filtration facility, by maintaining a zeta potential of approximately 14 mV(19), has been one instance where successful control using electrokinetic measurements has been applied. Bearing in mind that zeta potential measurements are limited in ability to predict performance during filtration(24) without some prior correlation, success of such a means of control has the pre-requisite that the nature of the water quality (in the latter case, turbidity) does not change.

Although operational control of a facility employing cationic polyelectrolytes may be feasible by carrying out electrokinetic measurements, this is not the case with anionic polyelectrolytes applied to predominantly negatively charged suspensions(35), where such measurements may be completely worthless as a means of control. For example, Black _et al_(5), investigating the use of polyelectrolytes in destabilization of a kaolin clay suspension, found that with a cationic polyelectrolyte the response to electrokinetic measurements was such as to give adequate indication of the conditions for destabilization (see Figure 2.11a). However, with an anionic polyelectrolyte, although the optimum dosage to give lowest residual turbidity was well defined, there was no concomitant response with electrokinetic measurements, as shown in Figure 2.11b.

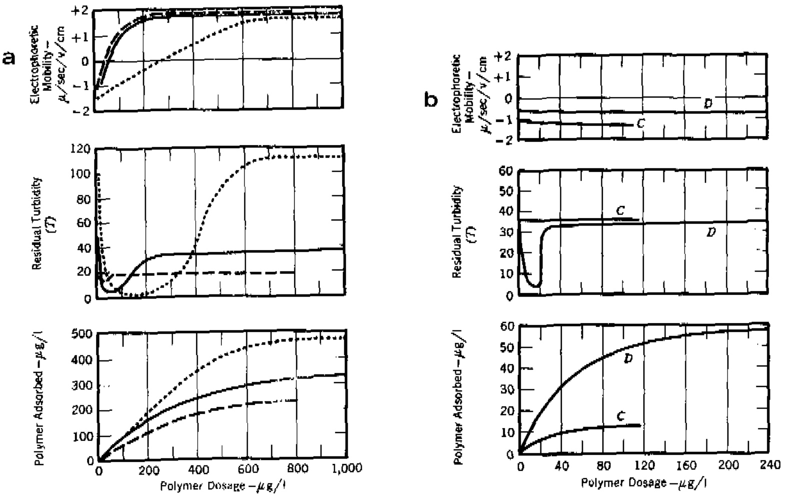


FIGURE 2.11: (a) Effect of Initial Clay Concentration on Destabilization of Kaolinite Clay Suspensions with Cationic Polymer PDADMA: The Dashed, Solid and Dotted Curves Represent Clay Concentrations of 14,9 mg l^{-1}, 29,8 mg l^{-1} and 73,2 mg l^{-1} respectively. (b) Effect of $CaCl_2$ on Destabilization of Kaolinite Clay Suspensions with Anionic Polymer HPAM-30: The Kaolinite Clay Suspensions (Concentration 33,3 mg l^{-1}) Contain 25,0 mg l^{-1} $CaCl_2$ (Curve C) and 250 mg l^{-1} $CaCl_2$ (Curve D). {From Black _et al_(5), With Permission of the American Water Works Association}

The above discussion has run a natural course to the following conclusion: Although the value of electrokinetic measurements in research applications is very evident(1, 4, 6, 26), optimum conditions for destabilization in practical applications may ultimately only be adequately predicted at present by techniques such as the standard jar test (see Chapter 8). Subsequent usage of electrokinetic measurements for control purposes is possible in certain cases after adequate correlation with jar test or filtration results etc.

The remainder of this chapter will discuss three different types of electrokinetic measurements and will present, where possible, typical results for different waters. The three types of measurements dealt with here are electrophoresis, streaming current and colloid titration.

2.8.2 Electrophoresis Measurements

Electrophoresis refers to the movement of a charged particle suspended in a fluid induced by an applied electrical force. When a direct current electric field is applied across a suspension containing particles with a nett double layer charge, the particles will migrate to the positive or negative pole depending on whether the particles carry a negative or positive charge respectively. Counter ions surrounding the colloid will migrate in the reverse direction of the particles.

In measurements of electrophoresis, the technique essentially comprises visual observation of the suspension through a microscope and timing a number of particles travelling a given distance under an applied electric field. A commonly used commercially available equipment for measuring electrophoretic mobility comprises(29, 36): (i) a stereoscopic microscope with ocular micrometer, 15 x eyepieces and 2x, 4x, 6x and 8x (adjusted magnification) objectives; (ii) a special illuminator capable of producing a thin beam of intense blue-white light, with a heat absorbing filter; (iii) a d.c. power supply, continuously variable from 0 to 500v; (iv) a clear plastic electrophoresis cell equipped with platinum-iridium electrodes; (v) a cell holder consisting of a thick and highly reflective mirror directing the light 45° upward through the tube of the cell and (vi) an interrupted-type cumulative reading electrical timer, reading in 0,1 seconds. The electrophoresis cell consists(29) essentially of a clear plastic block with a small polished tube extending through the centre. The tube is connected by two tapered ports to two solution chambers, within which are positioned the platinum-iridium electrodes.

Before carrying out measurements of electrophoresis it is necessary to calibrate the particular cell in use to compensate for the effect of electroosmosis(8, 29): a liquid in contact with a surface such as glass may possess a potential with respect to the latter. When an electric field is applied to such a system, there will be movement of the liquid along the walls of the cell in one direction and along the centre of the cell in the other direction. There is a layer at a fixed distance from the walls of the cell where the flow of liquid is zero. It is at this stationary layer where particles should be observed and electrophoretic mobilities taken.

Black et al(8) describe a procedure for calibrating a rectangular type electrophoresis cell of the Briggs type, which consists of measuring the mobilities of a standard suspension (polyvinyl chloride microspheres) at different positions in the cell, plotting the mobility profile and thus determining the mean velocity for the cell. The position in the cell at which the mean velocity occurs defines the stationary layer. Riddick(29) gives a value of 15% tube diameter as defining the position of the stationary layer from the wall of a tube type electrophoresis cell.

Electrophoretic mobilities may be converted to zeta potential using expressions concomitant with particle size and electrolyte concentration(11, 20). However, because of difficulties in assigning values to various terms in the appropriate equations, the calculated zeta potential may differ significantly from the true value(10). For this reason many workers express results solely in terms of electrophoretic mobility, rather than convert to zeta potentials.

With regard to control of destabilization of clay turbidity, the zeta potential or mobility value giving lowest residual turbidity depends on the type and concentration of clay, primary coagulant and flocculant aid used respectively. Using aluminium sulphate, the values of electrophoretic mobility corresponding to minimum residual turbidity in general range from -0,5 to -2,0 μ s^{-1} V^{-1} cm^{-1}(3,6). However, in some cases, although residual turbidity has a sharply defined minimum at optimal operating conditions, no accompanying response in electrophoretic mobility value is evident. As previously stated, this severely limits the utility of electrophoresis as a means of control without prior verification that changes in destabilization efficiency are accompanied by appreciable changes in zeta potential.

Using polyelectrolytes to destabilize clay dispersions, electrophoretic mobility values appear to be within a range similar to that using metal coagulants (for example, see Figure 2.11(5)).

For the case of organic colour removal using metal coagulants, optimum conditions giving lowest residual colour generally coincide with mobilities near zero(4) - but seldom exactly zero(32). Using a cationic polyelectrolyte to remove organic colour (humic and fulvic acids), again, electrophoretic mobilities of approximately zero have been reported(22) as coinciding with lowest residual colour.

During the lime-soda softening process, using flocculants to aid aggregation of the precipitates formed, the response of electrophoretic mobility to the condition of optimum flocculation of precipitates is dependent on the type of flocculant used(2): With activated silica data shows that a sharp peak of the already negative mobility occurs at the point of lowest residual turbidity; using a high molecular weight anionic polyacrylamide, mobility data does not define optimum flocculation conditions; with potato starch, which is a nonionic polymer, mobilities are completely unaffected by flocculant dosage and, with a high molecular weight cationic polyelectrolyte, optimum dosage is identified with zero mobility or the point of charge reversal of the suspension.

Destabilization of colloidal hydrous manganese dioxide with calcium(27) occurs when the extent of $Ca^{2\pm}$ sorption is sufficient to reduce the electrophoretic mobility of MnO_2 from approximately -3 to -1 $\mu S^{-1}V^{-1}cm^{-1}$; the mobility remaining at -1 $\mu S^{-1}V^{-1}cm^{-1}$ even at very high Ca^{2+} dosages i.e. neither charge reversal nor restabilization occurs.

From the above, one point is clearly evident: That is, in none of the examples cited have the conditions describing optimum performance coincided with zero particle surface charge. This lends support to statements made earlier that the mechanism of destabilization is usually more complex than that of simple charge neutralization.

2.8.3 Streaming Current Measurements

A disadvantage cited(33, 37) of electrophoretic measurements is that they are relatively lengthy and subjective, requiring visual observation and timing of individual particles. Streaming current measurements, on the other hand, have the advantage of speed and are not as subjective as tests of electrophoresis. Furthermore, with the streaming current technique, results obtained are immediately in terms of the average for the system.

The streaming current technique(11, 33, 37) involves placing a sample in a special cylinder containing electrodes at the top and bottom. A loose fitting piston is then partially submerged in the sample and reciprocated along its axis. Movement of liquid and counter-ions through the annular space between piston and cylinder creates a (streaming) current since the piston and bore assume the charge characteristics of the charged particles. The piston is connected to a synchronous motor and is driven at a set number of cycles per second thereby generating an alternating current. By connecting the motor to a synchronous rectifier and the electrodes to an amplifier, the alternating current is read on a direct current meter, with the polarity of output adjusted to indicate surface charge.

As with electrophoresis, although results may be expressed in terms of zeta potential, because of uncertainty of certain *constant* terms, values of streaming current (positive or negative) are usually presented.

Although streaming current measurements are relative and results depend on the particular streaming current detector used, in general it would appear that optimum conditions for destabilization (verified with jar tests carried out with turbid-coloured waters, lime treatment of raw sewage and wastewater from the paper industry(33)) coincide approximately with the inflection point of the streaming current titration curve produced with the particular coagulant used. Generally, for clay (turbid) and coloured waters, streaming current values corresponding to optimum destabilization conditions range from near zero to -12 μA.

2.8.4 Colloid Titration

The colloid titration technique (18, 31, 37, 38, 40) essentially comprises neutralization of a charged colloidal dispersion by an equivalent amount of a colloid of opposite charge. An advantage of this technique over both electrophoresis and streaming current measurements is the ease and rapidity with which measurements are carried out, but without the need for specialized equipment.

The procedure is as follows(18, 31): (i) add 100 ml sample to a 250 ml Erlenmeyer flask (prepare also a 100 ml distilled water blank); (ii) Add 5 ml of 0,001N methyl glycol chitosan (standard positive colloid) to the sample; (iii) Add two drops of 0,1% toluidine blue indicator to the contents of the flasks; (iv) Titrate with 0,001N polyvinyl alcohol sulphate (standard negative colloid), using a microburette. The end point is indicated by a subtle colour change from light blue to bluish-purple. Since the colour change is time dependent, titration should be carried out as quickly as possible. The above procedure should also be carried out for the blank.

Depending on the suspension concentration, the above chemical quantities may need to be adjusted so that sufficient methyl glycol chitosan is added to neutralize the original suspension and leave a measurable excess.

Colloid charge, conveniently expressed as milli-equivalents per litre of positive or negative colloid charge, is given by:

$$\text{Charge (meq l}^{-1}) = \frac{(A-B)N(1000)}{V} \qquad (2.28)$$

Where A = volume of polyvinyl alcohol sulphate (PVSK) added (ml)

N = normality of PVSK (eg. 0,001N)

B = volume of PVSK added to blank (ml)

V = volume of sample (ml)

From comparative data(18, 40) there appears to be good correlation between the results of colloid titration and electrophoretic measurements - up to the point describing average zero surface charge. Beyond this point, mobility and colloid charge values diverge markedly. However, whether this divergence is due to inaccuracy in colloid charge or electrophoretic mobility determinations, it does not deter from the value of the colloid titration technique as a method of control of coagulation(*in cases where such a method of control is appropriate* - see Section 2.8.1) since, as pointed out before, prior correlation with, say, jar test results are in any case necessary.

It appears that with clay turbidity removal the colloid charges corresponding to optimum conditions of destabilization are within the range -25.10^{-4} to $+300.10^{-4}$ meq l^{-1}(18, 40). With colour removal from surface waters the range appears to be from -200.10^{-4} to $+200.10^{-4}$ meq l^{-1}(18).

It should be noted that although colloid titration measurements are carried out readily, the limitations of electrokinetic measurements in general as discussed earlier, are still applicable. For example, TeKippe and Ham(38) found that with the coagulation of silica particles with alum, the results from colloid titration experiments had no correlation with either jar test or pilot scale filtration experiments. This further supports previous statements indicating that the applicability of electrokinetic measurements as a means of control of the coagulation process depends very largely on the type of suspension.

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3

Coagulants

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3.0 INTRODUCTION

In the previous Chapter, properties of colloids in suspension were dealt with: The effect of the surface charge carried by the colloids was presented and the stability of hydrophobic colloids in terms of the electrical double layer produced by the charged interfaces was discussed. Destabilization of such particles by simple electrolytes was dealt with in terms of a model describing repression of the electrical double layer. A very important point emphasized in Chapter 2 was that there are other mechanisms besides charge neutralization involved in colloid destabilization which, in some cases, may be dominant during destabilization. These mechanisms, to be described in later Chapters, are promoted by coagulants other than those which may be described as simple electrolytes. Such coagulants include those given the general name *metal coagulants* and *polyelectrolytes*.

The objective of this Chapter is to present a description of commonly used metal coagulants (Section 3.1) and polyelectrolytes (Section 3.2) and, for each, to discuss what happens, as it were, from the instant of coagulant addition to the suspension, to the onset of destabilization. Mechanisms of destabilization effected by such coagulants, for different substances in suspension or solution will be presented in later Chapters.

3.1 METAL COAGULANTS

3.1.1 Commonly Used Metal Coagulants

The commonly used metal coagulants fall into two general categories: those based on aluminium and those based on iron. The aluminium coagulants include aluminium sulphate, aluminium chloride, polyaluminium chloride and sodium aluminate. The iron coagulants include ferric sulphate, ferrous sulphate, chlorinated copperas and ferric chloride. Other chemicals used as coagulants include hydrated lime, $Ca(OH)_2$ and magnesium carbonate, $MgCO_3$.

The popularity of aluminium and iron coagulants arises not only from their effectiveness as coagulants but also from their ready availability and relatively low cost. The efficacy of these coagulants arises principally from their ability to form multi-charged polynuclear complexes in solution with enhanced adsorption characteristics. The nature of the complexes formed may be controlled by the pH of the system (see section 3.1.2).

The following presents a summary of some of the relevant chemical and physical properties of aluminium and iron coagulants. It should be noted that the chemical equations presented are only intended to portray a general idea of the reactions which occur. The hydrolysis reactions of iron and aluminium salts are far more complicated - as will be seen in later sections - than the following suggests. Furthermore, in many cases of destabilization, the reactions do not necessarily proceed to equilibrium, as shown here, before destabilization has occurred.

3.1.1.1 Aluminium Sulphate - $Al_2(SO_4)_3.14H_2O$

Aluminium sulphate, probably the most widely used coagulant, is manufactured from the digestion of bauxite or aluminium ores with sulphuric acid. The quantities of bauxite used are just over the stoichiometric amounts needed to combine with the acid, so that in the final product no free acid is present. Evaporation of water in the process results in the dry product having the approximate formula $Al_2(SO_4)_3.14H_2O$ and with an aluminium oxide (Al_2O_3) content ranging from 14% to 18% (m/m).

Dry aluminium sulphate may be supplied as slabs, kibbled and screened, or kibbled and ground. Slabs are blocks about 600 mm x 180 mm x 150 mm, weighing approximately 25 kg. The Al_2O_3 content is 14%. Slabs are used in water and wastewater treatment where a continuous dissolving system is required: They are sometimes placed in a sedimentation tank feed channel where they are readily dissolved in the stream of water or effluent - this procedure, although obviously not the most efficient in terms of coagulant usage, may be feasible for very small plants or in some cases as an emergency measure.

The kibbled and screened product, supplied in 50-100 kg jute bags, is broken down to pieces of approximately 80 mm and less with the fines removed by screening. The Al_2O_3 content is 16%. This grade is appropriate where dissolution is carried out without agitation: absence of fines prevents a troublesome paste forming on the bottom of the dissolution tank.

The kibbled and ground products, supplied in 50-100 kg jute bags (kibbled) or 50 kg paper sacks (ground), are used when dissolution is carried out with agitation or by heat.

Liquid alum is usually supplied in 20 tonne tanker loads or, where appropriate, by railroad tanker.

It is produced by withdrawal before evaporation proceeds as far as the dry product, and is standardized at 8% Al_2O_3, which is approximately equivalent to a 50% solution of the dry product.

The dry product may be stored in concrete, iron or steel tanks. Liquid aluminium sulphate, or solutions of the dry product are corrosive and need to be stored in lead, rubber, plastic or epoxy lined steel, or stainless steel tanks. An inexpensive installation may use a plastic *bag* supported in a wooden or steel tank(14). pH values of various concentrations of aluminium sulphate solutions are shown in Figure 3.1(2).

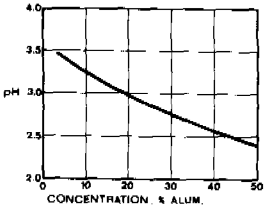


FIGURE 3.1: pH of Solutions of Commercial Dry Aluminium Sulphate (17% Al_2O_3 in Dry Alum).

Assuming that reactions of aluminium sulphate in water proceed to the electroneutral precipitate, $Al(OH)_3$ (which, as stated earlier, is not necessarily the case) a general idea of the reactions of aluminium sulphate with common alkaline reagents is given below:

$$\begin{aligned}
Al_2(SO_4)_3(H_2O)_{14} + 6OH^- &= 2Al(OH)_3 + 3SO_4^{2-} + 14H_2O \\
Al_2(SO_4)_3(H_2O)_{14} + 6Ca(HCO_3)_2 &= 2Al(OH)_3 + 3CaSO_4 + 6CO_2 + 14H_2O \\
Al_2(SO_4)_3(H_2O)_{14} + 6NaHCO_3 &= 2Al(OH)_3 + 3Na_2SO_4 + 6CO_2 + 14H_2O \\
Al_2(SO_4)_3(H_2O)_{14} + 3Na_2CO_3 &= 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2 + 14H_2O \\
Al_2(SO_4)_3(H_2O)_{14} + 6NaOH &= 2Al(OH)_3 + 3Na_2SO_4 + 14H_2O \\
Al_2(SO_4)_3(H_2O)_{14} + 3Ca(OH)_2 &= 2Al(OH)_3 + 3CaSO_4 + 14H_2O
\end{aligned}$$

3.1.1.2 Aluminium Chloride - $AlCl_3.6H_2O$

Aluminium chloride is normally supplied in solution form containing 20% Al_2O_3 with a pH and density of approximately 2,5 and 1 300 kg m^{-3} respectively. It has been widely used for sludge conditioning and has often been described as a good general purpose conditioner. Because of hydrochloric acid (HCl) released on hydrolysis, solutions need to be stored under similar conditions to ferric chloride (see below).

3.1.1.3 Polyaluminium Chloride
$(Al(OH)_{1,5}(SO_4)_{0,125}Cl_{1,25})_n$

This coagulant, a relatively new product developed in Japan, is a partially hydrolysed aluminium chloride incorporating a small amount of sulphate. The results obtained with this coagulant are equivalent to using aluminium sulphate in conjunction with a polyelectrolyte, although neither the precise chemical nature of the product nor the reason for its enhanced performance is perfectly understood(17). Approximately half the dosage is required for turbidity removal, but more or less the same dosage as aluminium sulphate is required for predominantly coloured waters. In cases where waters are predominantly turbid, therefore, use of this coagulant may significantly reduce sludge disposal problems. Polyaluminium chloride is supplied as a liquid with the equivalent of 10% Al_2O_3. Diluted solutions of concentration 0,4 - 3% show evidence of slow hydrolysis.

3.1.1.4 Sodium Aluminate - $NaAlO_2$

Sodium aluminate differs from alum in that it is alkaline rather than acidic in its reactions. It is rarely used alone, but generally with alum to obtain some special result. For example, in the coagulation of highly coloured waters, alum (plus acid usually) is added to the water to coagulate the colour at its requisite low pH - this, however, results in undesirable concentrations of soluble aluminium compounds; alkaline sodium aluminate is then added - also lime if required - to increase the pH to at least 6,0 which causes the soluble aluminium to precipitate out in a secondary settling basin.

The reactions of $NaAlO_2$ with $Al_2(SO_4)_3(H_2O)_{14}$ and with free CO_2 produce insoluble aluminium compounds, viz,

$$6NaAlO_2 + Al_2(SO_4)_3(H_2O)_{14} = 8Al(OH)_3 + 3Na_2SO_4 + 2H_2O$$

$$2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3$$

$NaAlO_2$ is also used in the lime-soda softening process as an aid in flocculating the fine precipitates of calcium carbonate and magnesium hydroxide resulting from the softening reactions.

$NaAlO_2$ may be purchased either as a solid or as a solution. The cost of the material is high but the required doses are small.

3.1.1.5 Ferric Sulphate - $Fe_2(SO_4)_3.8H_2O$

This is available in solid or liquid form. In the solid form the material is granular and free flowing with the following typical specifications: 72/75% m/m $Fe_2(SO_4)_3$ and 20/21% m/m Fe^{3+}. In the liquid form typical specifications are 40/42% m/m $Fe_2(SO_4)_3$ and 11,5% m/m Fe^{3+}. Lower purity liquid grades are available with 30% m/m $Fe_2(SO_4)_3$ content.

In general, all ferric coagulants are used over a wide range of pH from 4,0 to 11,0. Ferric sulphate is particularly useful when used for colour removal at low pH values and also at high pH values where it is used for iron and manganese removal, and in the softening process. For the latter uses the insolubility of the ferric hydroxides at high pH values make the iron coagulants in general preferable to alum.

The comments on the chemical equations relating to alum are also applicable to all the following equations:

$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 = 2Fe(OH)_3 + 3CaSO_4 + 6CO_2$

$Fe_2(SO_4)_3 + 6NaHCO_3 = 2Fe(OH)_3 + 3Na_2SO_4 + 6CO_2$

$Fe_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 3Na_2SO_4 + 3CO_2$

$Fe_2(SO_4)_3 + 6NaOH = 2Fe(OH)_3 + 3Na_2SO_4$

$Fe_2(SO_4)_3 + 3Ca(OH)_2 = 2Fe(OH)_3 + 3CaSO_4$

3.1.1.6 Ferrous Sulphate - $FeSO_4.7H_2O$

Also known as copperas (although the latter term is falling into disuse) ferrous sulphate is available either as crystals or granules containing 20% Fe, both of which are readily soluble in water. Ferrous sulphate reacts either with natural alkalinity or added alkalinity to form ferrous hydroxide - $Fe(OH)_2$, but since ferrous hydroxide is relatively soluble, it must be oxidized to ferric hydroxide in order to be useful. At pH values above 8,5 oxidation may be accomplished by (i) aeration; (ii) by the dissolved oxygen in the water, or, (iii) by adding chlorine. For (i) and (ii) lime must be added to obtain sufficient alkalinity.

The important reactions for ferrous sulphate are:

$FeSO_4(H_2O)_7 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4 + 7H_2O$

$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$

Ferrous sulphate and lime find their greatest use at high pH values; for example, the lime-soda softening process and in iron and manganese removal.

3.1.1.7 Chlorinated Ferrous Sulphate

When chlorine is used to oxidize the ferrous hydroxide obtained from ferrous sulphate, the process is known as the chlorinated copperas treatment. In contrast to the high pH values required for oxidation by oxygen, chlorine will react over a wide pH range.

In practice ferrous sulphate and chlorine are fed separately and are generally mixed just prior to entry into the coagulation system. The reaction with chlorine produces ferric sulphate and ferric chloride and each mg/l of ferrous sulphate theoretically requires 0,13 mg/l of chlorine, although an excess of chlorine is generally added to ensure complete reaction and to provide chlorine for disinfection purposes.

The reaction is as follows:

$$6FeSO_4(H_2O)_7 + 3Cl_2 = 2Fe_2(SO_4)_3 + 2FeCl_3 + 7H_2O$$

Coagulation with chlorinated copperas (or ferrous sulphate) is especially useful where pre-chlorination is required. It has the further advantage over ferrous sulphate in that coagulation may be obtained over a wide range of pH values: 4,0 to 11,0.

3.1.1.8 Ferric Chloride - $FeCl_3$

Ferric chloride is available commercially in the liquid, crystal or anhydrous forms. The liquid and crystal forms are very corrosive and must be handled in a similar fashion to hydrochloric acid: for example, steel lined with fiberglass re-inforced polyester, PVC, epoxy resin, polyethylene, polypropylene, rubber or glass etc. Polyamide type plastics are not suitable. The liquid grade is supplied as a 43% $FeCl_3$(m/m) solution(9). The anhydrous form may be stored in steel tanks but only if moisture is excluded. Because ferric chloride is very hygroscopic, drums must remain sealed until needed and their entire contents must be dissolved at one time.

The reactions of ferric chloride with natural or added alkalinity may be written as follows:

$$2FeCl_3 + 3Ca(HCO_3)_2 = 2Fe(OH)_3 + 3CaCl_2 + 6CO_2$$

$$2FeCl_3 + 3Ca(OH)_2 = 2Fe(OH)_3 + 3CaCl_2$$

3.1.1.9 Dissolution of Dry Coagulant Products

Lump or ground coagulant products may be dissolved in batch fashion or continuously. With a batch method the appropriate quantity of chemical (either preweighed or a number of bags) is dissolved in a tank, usually with a mechanical mixer, then fed either directly or after dilution to the rapid mixing facility (see Chapter 6). Feeding may be carried out via, for example, an adjustable orifice or metering pumps.

With a continuous method, dry granular chemical is fed continuously, by means of a screw or vibrating feeder etc., from a hopper to a dissolving tank. The dissolving tank may be fitted with a mechanical mixer, or dissolution may be carried out in simulated plug flow fashion, as shown in Figure 3.2.

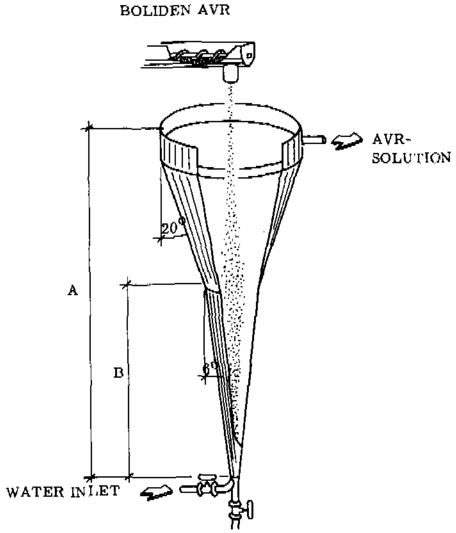


FIGURE 3.2: Continuous Counter-Flow Coagulant Dissolution System. (Courtesy Boliden).

3.1.2 Chemistry of Metal Coagulants

3.1.2.1 Hydration and Stepwise Substitution Reactions

Having identified the common metal coagulants, the following discussions are devoted to the reactions taking place when metal coagulants are introduced into the stream of water to be treated.

Aluminium and ferric salts, when in solution, immediately dissociate to form hydrated reaction products. The metal ions form coordination compounds(3, 4, 15) with water molecules to give $\{Al(H_2O)_6\}^{3+}$ and $\{Fe(H_2O)_6\}^{3+}$. These species, referred to as the trivalent ions of aluminium and iron, are often presented as Al^{3+} and Fe^{3+} for reasons of convenience in presentation.

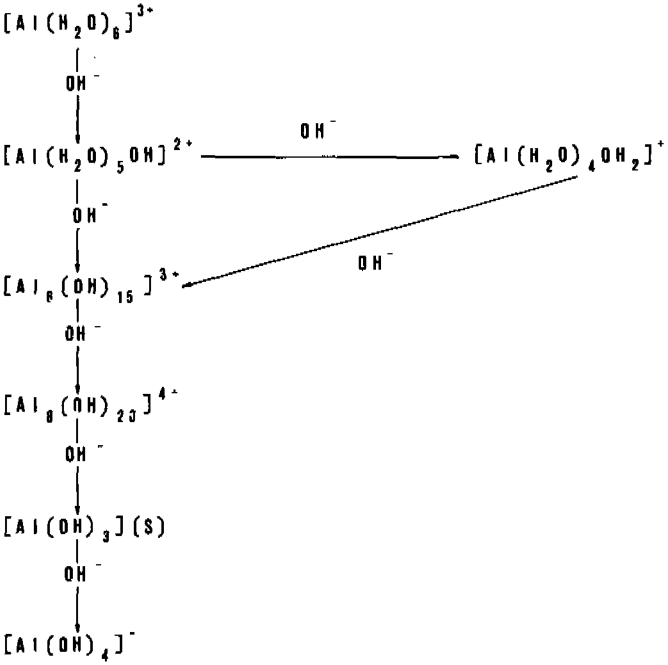
In solution there will also be other ligands and a stepwise substitution of the ligand molecules or ions, for the water molecule takes place. The extent of this substitution depends on the concentration of the substituted ligand. For the destabilization of hydrophobic colloids with iron and aluminium coagulants, the complexes of principal interest are those comprising H_2O and OH^- as ligands. The OH^- ligands may be thought of as arising from the dissociation of bound H_2O ligands *or* from the replacement of H_2O by OH^- ligands. It can be seen that in either case, the extent to which OH^- ions are bound to the metal complex is dependent primarily on the pH or the concentration of OH^- ions in solution.

The scheme of these stepwise substitution reactions for Al(III) is shown in Table 3.1 below(21). From say the first reaction, one can write:

$$\{Al(H_2O)_6\}^{3+} \rightleftharpoons \{Al(H_2O)_5OH\}^{2+} + H^+$$

from which it is seen that complexes of metal ions in water act as weak acids. Aluminium salt solutions show pH values similar to those of equimolar acetic acid solutions. The first ionization constant (K_1) of the aquo-ferric ion is

TABLE 3.1 SCHEME OF STEPWISE HYDROLYSIS REACTIONS FOR ALUMINIUM



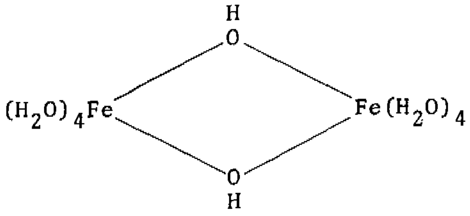
similar to that of phosphoric acid (i.e. a 10^{-3} M solution of $FeCl_3$ has a pH of about 3.2).

The donor capacity of a ligand is frequently not *exhausted* by being co-ordinated to a metal ion and there is a possibility of it forming a co-ordinative bond with another metal ion. The ligand thus acts as a *bridge* between the two central ions. Both unidentate and multidentate ligands may serve as bridges in polynuclear complexes.

Both iron and aluminium-hydroxo complexes have pronounced tendencies to form polynuclear complexes. The simplest reaction leading to a bi-nuclear iron complex species is:

$$2\{Fe(H_2O)_5(OH)\}^{2+} = \{Fe_2(H_2O)_8(OH)_2\}^{4+} + 2H_2O$$

The bi-nuclear ion so formed has sufficient stability to exist in appreciable concentrations in iron solutions which are more concentrated than 10^{-4}M. The two metal ions are thought to be bound by two hydroxo bridges:



3.1.2.2 *Stability of Metal-Ion Hydrolysis Species*

The stepwise formation of metal-ion hydrolysis species can be described by a set of stability constants. The individual stability constants cannot be directly calculated and to obtain them it is necessary to find a suitable relationship between the individual constants (or their products) and the experimentally measurable parameters, as exemplified for mononuclear species below(4):

The total concentration of the central metal ion (T_{Me}) and of the ligand (T_L) are known.

T_{Me} is the sum of the concentrations of the different species containing it:

$$T_{Me} = \{Me\} + \{MeL_1\} + \ldots\ldots\ldots\ldots + \{MeL_N\} = \sum_{i=0}^{N} \{MeL_i\}$$

where L is the ligand.

The total concentration of the ligand is the weighted sum of the species concentrations containing it:

$$T_L = \{L\} + \{MeL\} + 2\{MeL_2\} + \ldots\ldots\ldots\ldots + N\{MeL_N\}$$

$$= \{L\} + \sum_{i=1}^{N} i\{MeL\}$$

Further

$$K_1 = \frac{\{MeL\}}{\{Me\}\{L\}}$$

$$K_2 = \frac{\{MeL_2\}}{\{MeL\}\{L\}}$$

$$\vdots$$

$$K_N = \frac{\{MeL_N\}}{\{MeL_{N-1}\}\{L\}}$$

where K is the stability constant
and

$$\beta_1 = K_1 = \frac{\{MeL\}}{\{Me\}\{L\}}$$

$$\beta_2 = K_1K_2 = \frac{\{MeL_2\}}{\{Me\}\{L\}^2}$$

$$\vdots$$

$$\beta_N = K_1K_2 \ldots\ldots\ldots\ldots\ldots K_N = \frac{\{MeL_N\}}{\{Me\}\{L\}^N}$$

where β is known as the overall stability constant.

Values of stability constants K for some hydrolysis reactions with iron and aluminium are given in Table 3.2 below(21). From such stability constants, the concentration (or fraction present) of each species in solution under equilibrium conditions may be computed (see later).

TABLE 3.2: STABILITY CONSTANTS FOR IRON AND ALUMINIUM(21)

REACTION	log K (25°C)
$[Fe(H_2O)_6]^{3+} + H_2O = [Fe(H_2O)_5OH]^{2+} + H_3O^+$	-2,17
(Note: H_2O molecules are omitted from subsequent reactions for brevity)	
$[Fe(OH)]^{2+} + H_2O = [Fe(OH)_2]^+ + H^+$	-4,7
$2[Fe(OH)]^{2+} = [Fe_2(OH)_2]^{4+}$	1,46
$Fe^{3+} + 3H_2O = Fe(OH)_3(S) + 3H^+$	-6
$Fe(OH)_3(S) + H_2O = [Fe(OH)_4]^- + H^+$	-18,5
$Al^{3+} + H_2O = [Al(OH)]^{2+} + H^+$	-5,03
$Al^{3+} + 3H_2O = Al(OH)_3(S) + 3H^+$	-9,1
$2Al^{3+} + 2H_2O = [Al_2(OH)_2]^{4+} + 2H^+$	-6,27
$Al(OH)_3(S) + H_2O = [Al(OH)_4]^- + H^+$	-12,74
$6Al^{3+} + 15H_2O = [Al_6(OH)_{15}]^{3+} + 15H^+$	163

3.1.2.3 Average Co-Ordination Number

The extent of complex formation may be characterized by the *average co-ordination number*, (or formation function) $\bar{n}$ (see also Section 3.1.2.4).

$$\text{Where } \bar{n} = \frac{\text{concentration of ligands bound to metal ions}}{\text{total metal ion concentration}}$$

$$= \frac{T_L - \{L\}}{T_{Me}}$$

where {L} is the *free* ligand concentration.

The average co-ordination number is determined experimentally by alkalimetric titration. The procedure is illustrated by an example below(21): To an $Al(ClO_4)_3$ (aluminium perchlorate) solution NaOH (sodium hydroxide) is incrementally added. After each addition of NaOH the pH of the solution is determined with a glass electrode and hence the hydrogen ion concentration of the solution may be determined.

It will be assumed that together with free Al^{3+} ions, the mononuclear complexes $Al(OH)^{2+}$ and $Al(OH)_3$ are formed together with polynuclear complexes collectively given by $Al_n(OH)_x^{3n-x}$.

The total aluminium concentration *at any given pH* is given by:

$$Al_T = \{Al^{3+}\}+\{Al(OH)^{2+}\}+\{Al(OH)_3\}+ \Sigma n\{Al_n(OH)_x^{3n-x}\}$$

$$= \frac{\{ClO_4^-\}}{3} \qquad (3.1)$$

For electroneutrality at any given pH:

$$3\{Al^{3+}\}+2\{Al(OH)^{2+}\}+ \Sigma(3n-x)\{Al_n(OH)_x^{3n-x}\}+\{Na^+\}+\{H^+\}$$

$$= \{ClO_4^-\}+\{OH^-\} \qquad (3.2)$$

From the addition of one mole of NaOH, one mole of Na^+ and one mole of OH^- are formed.

Hence

$$\{Na^+\} = \{OH^-\} \text{ added}$$

Combining equations (3.1) and (3.2):

$$3\{Al^{3+}\}+3\{Al(OH)^{2+}\}+3\{Al(OH)_3\}+\Sigma 3n\{Al_n(OH)_x^{3n-x}\}$$

$$= 3\{Al^{3+}\}+2\{Al(OH)^{2+}\}+\Sigma(3n-x)\{Al_n(OH)_x^{3n-x}\}+\{OH^-\}\text{added} +\{H^+\}-\{OH^-\}$$

i.e.

$$\{OH^-\}\text{added} +\{H^+\}-\{OH^-\} = \{Al(OH)^{2+}\}+3\{Al(OH)_3\}+\Sigma x\{Al_n(OH)_x^{3n-x}\}$$

Studying the righthand side of the above equation one sees that each term gives the moles of OH^- bound to each species. Hence the concentration of OH^- ions bound to aluminium is given by the r.h.s. of the above equation - and consequently by the l.h.s. Since all the terms of the l.h.s. are known the $\{OH^-\}_{bound}$ may be computed.

Hence for the above case the average co-ordination number $\bar{n}$ is given by:

$$\bar{n} = \frac{\{OH^-\}_{bound}}{\{Al_T\}}$$

$$= \frac{\{OH^-\}_{added} +\{H+\}-\{OH^-\}}{\{Al_T\}}$$

From this number, the mean charge of the total aluminium species may be found (at any particular pH).

i.e.

Mean charge = $(3-\bar{n})$

Hence if there is an *average* of, say, three OH^- ions bound per aluminium ion, then the *mean* charge of all the complex species will be zero. This is the isoelectric point. It can be said that the charge found above has a statistical character. The isoelectric point of the above solution may then be defined as the pH at which equal quantities of the aluminium species migrate to the anode and cathode of an electrophoretic cell.

If curves are drawn of pH versus the average co-ordination number $\bar{n}$ or the mean charge $(3-\bar{n})$, valuable information may be gleaned concerning the nature of the complexes present at any particular pH. As exemplified in Figure 3.3(21), one can see that for aluminium between pH 10 and 10,5 for instance, the constant value of $\bar{n} = 4$ indicates that a definite compound (aluminate $\{Al(OH)_4\}^-$ or $\{Al_2(OH)_7\}^-$) is formed.

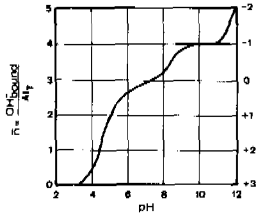


FIGURE 3.3: Values of Average Co-ordination Number $\bar{n}$, for Different pH Values. (Adapted From Stumm and Morgan(21)).

3.1.2.4 Species Distribution During Destabilization

Figures 3.4 (a) and (b) (taken from Stumm and O'Melia(22)) respectively show the concentrations of species present at different pH values for iron and aluminium solutions *at equilibrium*. The values are derived from stability constants such as those shown in Table 3.2. The cross-hatched areas indicate the range of coagulant dosages which are normally used in water treatment. From these figures one might be tempted to conclude that the species involved in coagulation are the insoluble metal hydroxide precipitates. Although precipitation reactions are of doubtless importance in certain cases: for example during organic colour removal, phosphorus removal in tertiary wastewater treatment processes and removal of iron, destabilization reactions are often other than that of precipitation: The rate of transition

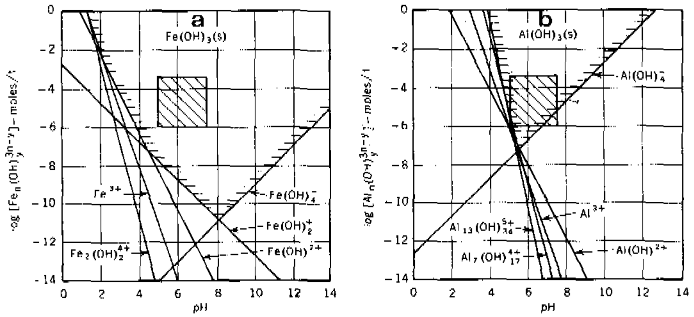


FIGURE 3.4: Equilibrium-Solubility Domains of (a) Ferric Hydroxide and (b) Aluminium Hydroxide in Water. These Diagrams Have Been Calculated Using Representative Values for the Equilibrium Constants for Solubility and Hydrolysis Equilibria. Shaded Areas are Approximate Operating Regions in Water Treatment Practice; Coagulation In These Systems Occurs Under Conditions of Over-Saturation With Respect to the Metal Hydroxide. (From Stumm and O'Melia(22), with permission of the American Water Works Association

from aquo metal ions to metal hydroxide precipitates is dependent on the pH and applied concentration of the solution. For the concentrations used in water treatment, true equilibrium - as shown in Figures 3.4 (a) and (b) - may in some cases require time spans longer than required to attain destabilization. For this reason the use of stability constants in identifying the species effective during destabilization in water treatment processes may not be valid.

Singley and Black(19), Sullivan and Singley (23) and Singley and Sullivan(20) attempted to identify the probable species present during destabilization by using the concept of average co-ordination number $\bar{n}$, described in Section 3.1.2.3.

They recognized that during the time required for alkalimetric titrations a quasi-equilibrium condition was attained for which the mass-action relationship is best referred to as an *instantaneous concentration quotient Q*. For example, in the general reaction

$$Fe^{3+} + nH_2O \rightleftharpoons Fe(OH)_n^{3-n} + nH^+$$

then Q may be defined as:

$$Q_n = \frac{\{Fe(OH)_n\}^{3-n}\{H^+\}^n}{\{Fe^{3+}\}}$$

That is, Q is equivalent to an instantaneous stability constant.

In their analysis they considered mononuclear species only, that is, in the case of iron, the species present were assumed to be:

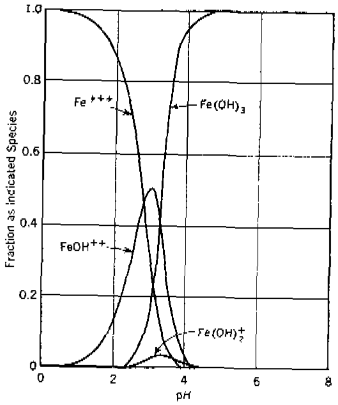
$$\{Fe^{3+}\};\ \{Fe(OH)^{2+}\};\ \{Fe(OH)_2^+\};\ \{Fe(OH)_3\};\ \{Fe(OH)_4^-\};\ \{Fe(OH)_5^{2-}\}$$

and $\{Fe(OH)_6^{3-}\}$

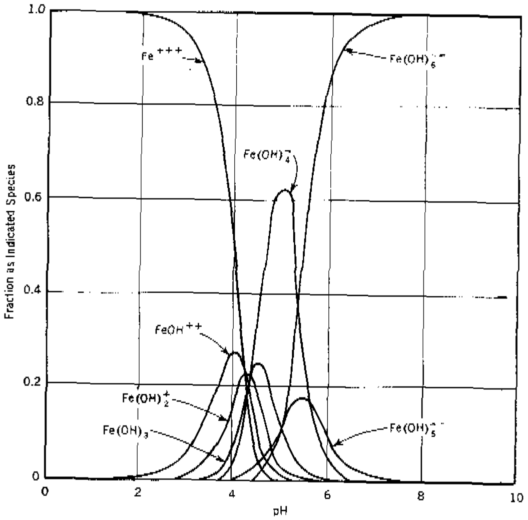
A maximum co-ordination number of 6 was assumed for both iron and aluminium. This is probably valid as a first approximation.

By setting up equations for each of the six concentration quotients, Q, and for the average co-ordination number, $\bar{n}$, it was possible to calculate the species present and their concentration at each pH value. Results for iron and aluminium are shown in Figures 3.5 (a)(20) and (b)(23) respectively. It is seen that in each case, as the concentration is reduced, the dominance of the electroneutral species $Fe(OH)_3$ and $Al(OH)_3$ reduces. If the concentration of coagulants applied is large enough and the pH of the solution is suitable, then polynuclear precipitates are dominant.

It should be noted that the mononuclear species considered above are a simplification, especially for the case of aluminium: when a quantity of aluminium salts are put into solution, then during progressive hydrolysis and substitution reactions numerous polymeric species are formed; the extent of polymerization becoming more pronounced as the charge of the metal species decreases. As shown in Figure 3.4.(b), eventually colloidal metal hydroxide polymers and insoluble metal-hydroxide precipitates may form, the

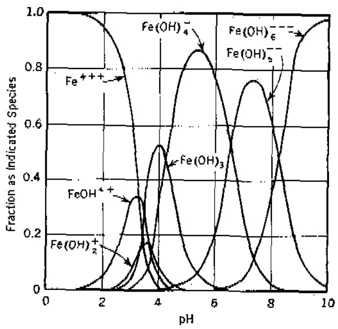


Distribution Diagram for Iron (III) Species for $Fe_T = 1 \times 10^{-3}$ M



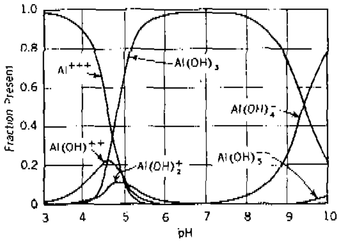
Distribution Diagram for Iron (III) Species for $Fe_T = 1 \times 10^{-5}$ M

a

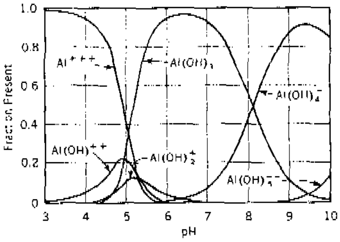


Distribution Diagram for Iron (III) Species for $Fe_T = 1 \times 10^{-4}$ M

b



Species Present as a Function of pH for 1×10^{-3} M Aluminum Perchlorate.



Species Present as a Function of pH for 1×10^{-4} M Aluminum Perchlorate.

FIGURE 3.5: (a) Species Distribution Diagrams for Iron (III) During Destabilization; (b) As for (a) But for Aluminium (III). {(a) From Singley and Sullivan(20) and (b) from Sullivan and Singley(23), with Permission of the American Water Works Association}

extent depending on the concentration of coagulant added (Figure 3.5 b) and whether destabilization reactions are such as to permit equilibrium conditions to be attained. At slightly acid or neutral pH values, positively charged or electroneutral metal-hydroxide polymeric colloids form, whereas at higher pH values, the polymerization of negative complexes takes place and negatively charged polymeric species are formed.

The polymerization action of metal coagulants, described above, is of high importance during destabilization since, as will be expanded in Chapter 4, it promotes an enhanced adsorption capacity of metal coagulant species to colloids.

It is seen that the mononuclear species model does not indicate the often reported (6, 12) Al: OH ratio of 1:2,5 for the predominant aluminium-hydroxide complex species during destabilization. Singley et al suggested that in systems from which the latter ratio has been reported, ligands other than OH^- were present which would give rise to species more complex than expected yet give an apparent coordination number, $\bar{n}$, of 2,5[23]. In the model of Singley et al the only ligands present were H_2O and OH^-.

Of interest from Figure 3.5(a) is that for $Fe_T = 10^{-4}$ M and at a pH of approximately 4,0, the predominant species is $Fe(OH)_3$, which is consistent with the conditions for organic colour removal. Although the mononuclear model suggested by Singley et al predicted closely their experimental results for iron solutions, this was not the case for aluminium solutions of concentration less than 10^{-5} to 10^{-4} M. The reason put forward was the probable formation of complicated polynuclear aluminium hydrolysis species at lower concentrations. The more complicated hydrolysis reactions of aluminium salt solutions is to a large part responsible for the narrower pH range often evident for optimum destabilization when compared with iron solutions. Furthermore, the different adsorption characteristics of aluminium hydrolysis species when compared with, say, iron coagulants or polyelectrolytes is a further indication of the complicated hydrolysis products formed: with iron salts and polyelectrolytes, adsorption follows a Langmuir adsorption isotherm, whereas with aluminium, adsorption often follows a Freundlich isotherm (See Section 2.3).

3.2 POLYELECTROLYTES

3.2.1 General

The term polyelectrolyte, as used here, refers to a large variety of natural or synthetic, water soluble, macromolecular compounds which have the ability to destabilize or enhance flocculation of the constituents of a body of water. Strictly speaking, the term *polymeric flocculants* is more appropriate as a general description, polyelectrolyte being perhaps better reserved for those carrying ionised groups. However, because of its widespread usage, the term polyelectrolyte will be taken as including those polymeric flocculants which are essentially non-ionic.

A polymer molecule may be described as a series of repeating chemical units held together by covalent bonds (polymer, from the literal Latin translation means many parts). If the repeating units are of the same molecular structure, the compound is termed a homopolymer. However, if the molecule is formed from more than one type of repeating chemical unit, it is termed a copolymer. The individual repeating units are called monomers and the molecular weight of the polymer molecule is the sum of the molecular weights of the individual monomers. The total number of monomer units is referred to as the degree of polymerization.

Polyelectrolytes are special classes of polymers containing certain functional groups along the polymer backbone which may be ionizable. If present, when the ionizable groups dissociate, the polymer molecules become charged either positively or negatively, depending on the specific functional groups present, and are thus referred to as cationic or anionic polyelectrolytes respectively. Polyelectrolytes that possess both positively and negatively charged sites are referred to as ampholytic, whereas those that possess no ionizable functional groups are termed nonionic polyelectrolytes. All polyelectrolytes are typical hydrophilic colloids. They have molecular weights generally in the range 10^4 to 10^7 and are soluble in water due to hydration of functional groups.

The following presents several types of polyelectrolytes currently in use. It is not intended as a comprehensive list but merely to provide a general picture of polyelectrolyte properties. The mechanisms of destabilization by polyelectrolytes are reserved for Chapter 5.

3.2.2 Activated Silica

Activated silica is probably the first polyelectrolyte to be used widely in water clarification. In preparing activated silica (which is an anionic polyelectrolyte) commercial sodium silicate solutions (pH approximately 12) in concentrations in excess of 2.10^{-3}M are neutralized with acid reagent (e.g. sulphuric acid, chlorine, aluminium sulphate or sodium bicarbonate) to a pH of less than 9. Under these conditions the silica solution is oversaturated with respect to amorphous silica and polymeric silicates, which are negatively charged kinetic intermediates in the transition to a silica precipitate, are formed. The reaction is stopped prior to precipitate formation by dilution to a concentration less than 2.10^{-3}M (compare this to the intermediate species formed during hydrolysis reactions of metal coagulants - Section 3.1.2).

Activated silica is commonly used at dosages of 1/15 to 1/10 the primary metal coagulant dosage (i.e. 2 to 5 mgl^{-1})(16). A disadvantage with this chemical is that with carelessness in the method of preparation (concentration of reagents, mixing, degree of neutralization, ageing etc.) silica gel may form. For this reason, the usage of activated silica often leads to blockages in pumps and feedpipes and may give rise to reduced filter runs(16, 18).

3.2.3 Natural Polyelectrolytes

Polyelectrolytes, although a comparatively recent term, have long been used as flocculants. Sanskrit literature (ca. 2000 B.C.) mentions the use of the crushed nuts of the Nirmali tree, *Strychnos potatorum* as a means of clarifying water(7); their action is most likely due to the presence of an organic water soluble polymer(16). Today, there are several such naturally derived substances used as polyelectrolytes, most of them being based on a polysaccharide skeleton with anionic properties due to the presence of carboxyl groups. Their molecular weight may be up to 10^5. An advantage of natural polyelectrolytes, especially for their use in potable water treatment, is that in general they are virtually toxic free. Examples are as follows:

3.2.3.1 Guar Gums

Neutral (non-ionic) polysaccharides relatively unaffected by pH and ionic strength. They are subject to enzymatic degradation on storage, but this may be prevented by the addition of citric or oxalic acid. Guar gum has been used in uranium ore processing;

3.2.3.2 Starches

Examples are processed polymers based on potato starch. These polyelectrolytes may be non-ionic, cationic or anionic, depending on the processing. The cationic types have quaternary ammonium group substitutions and the anionic types carboxylic substitutions;

3.2.3.3 Tannins

Complex polysaccharide tannin derivatives that have been used extensively in potable, wastewater and industrial effluent treatment applications. They are generally most effective under acidic conditions. Care must be taken on storage as they are subject to degradation reactions if left for lengthy periods.

3.2.3.4 Sodium Alginate

A completely non-toxic polyelectrolyte (widely used as a food additive) which is extracted from brown seaweed. The commercial product contains sodium and calcium carbonates. Sufficient Na_2CO_3 is present to allow a 0,5% solution to be prepared in waters containing up to 500 mg l^{-1} calcium (as $CaCO_3$). For higher concentration solutions or higher calcium concentrations, additional Na_2CO_3 may be added to precipitate $CaCO_3$ and thereby prevent the relatively ineffective calcium alginate from forming. When used as a flocculant aid, dosages are normally within the range 0,1 to 0,6 mg l^{-1}.

3.2.4 Synthetic Polyelectrolytes

Although natural polyelectrolyte products have the advantage of being virtually toxic free, the use of synthetic polyelectrolytes has gradually become more widespread. They are, in general, more effective as flocculants principally due to the possibility of controlling properties such as the number and type of charged units, molecular weight and so on.

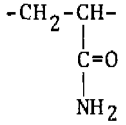
Because of the level of control possible during manufacture, synthetic polyelectrolytes have the potential of being applied almost in a *tailor-made* fashion. However, because of the general attitude of manufacturers(5, 13, 16), information required to achieve an adequate understanding of polyelectrolyte properties and performance in a particular application is seriously limited: such information being regarded as proprietary and not available either from product bulletins or directly from the manufacturers. Hence, a potential user of polyelectrolytes is faced with a multitude of products which must be evaluated on a trial and error basis to identify the most appropriate for the particular application. Furthermore, since most products are defined virtually solely by brand name or number, having identified a particular product valuable information concerning the type of polymer, degree of hydrolysis, molecular weight and so on, linked to the particular water constituents, is lost.

Packham(16) recommends that the *minimum* information which should be supplied by the manufacturer are as follows:

(i) type of polymer or copolymer;
(ii) concentration of active ingredient;
(iii) concentration of free monomer;
(iv) concentration and nature of other impurities;
(v) molecular weight or intrinsic viscosity under specified conditions;
(vi) proportion of ionizable groups and
(vii) amount of insoluble material present.

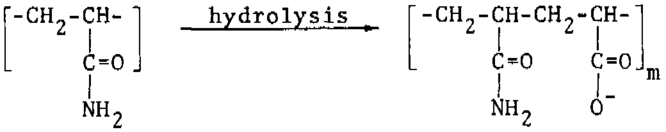
3.2.4.1 Structure of Synthetic Polyelectrolytes

A very high proportion of synthetic polyelectrolytes are based on polyacrylamide and its copolymers with polyacrylic acid. The acrylamide monomer, making up the units of the polymer, is prepared by reacting natural gas and methane at high temperatures in the presence of controlled amounts of oxygen and ammonia to form hydrocyanic acid and acetylene followed by catalysis with cuprous chloride. The acrylonitrile which results is then acid hydrolyzed to the acrylamide monomer using sulphuric acid. The acrylamide is then polymerized by catalysis. Polyacrylamide itself is nonionic but on hydrolysis the macromolecule aquires carboxyl groups and assumes an anionic character. Increased negativity is usually accomplished by copolymerizing acrylamide with acrylic acid. The structure of nonionic polyacrylamide is shown below:

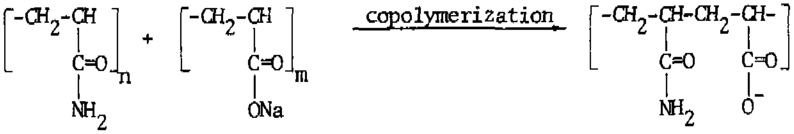


$$-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}-$$

The structure of anionic hydrolysed polyacrylamide is as follows:

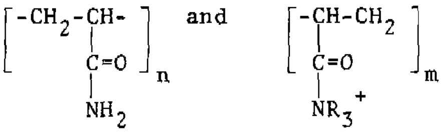


The structure of anionic polyacrylamide formed by copolymerization with sodium (or potassium or hydrogen) acrylate is as shown below:



The structures of anionic polyacrylamide formed by hydrolysis, and by copolymerization with acrylate are seen to be identical. However, with copolymerization more control over molecular weight distribution and charge density is possible.

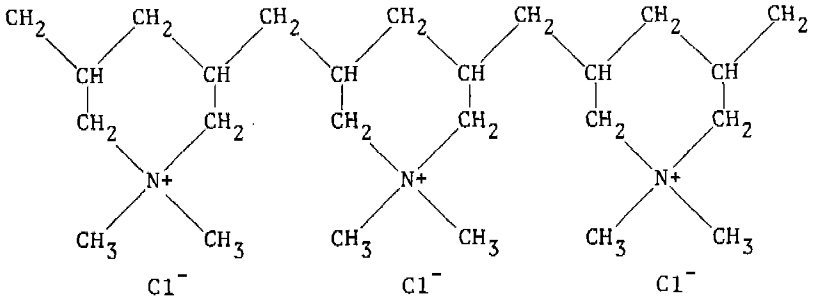
The percentage of acrylate units copolymerized is referred to as the *percent hydrolysis;* The higher the degree of hydrolysis, the higher is the overall ionic charge. Typically, percent hydrolysis ranges from zero to 30%. Cationic derivatives of polyacrylamide are available: for example, those produced by copolymerization of acrylamide and quaternary ammonium polyacrylamides, as shown below:



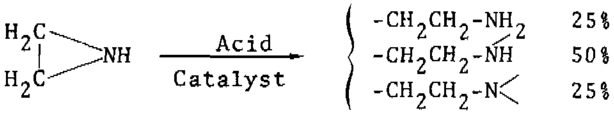
$$\left[\begin{array}{l}-CH_2-CH-\\ \qquad\quad |\\ \qquad\quad C=O\\ \qquad\quad |\\ \qquad\quad NH_2\end{array}\right]_n \quad \text{and} \quad \left[\begin{array}{l}-CH-CH_2\\ \quad |\\ \quad C=O\\ \quad |\\ \quad NR_3^{+}\end{array}\right]_m$$

Where R is usually a CH_4 or CH_3CH_2 derivative.

A common cationic quaternary ammonium compound is polydiallyldimethylammonium chloride, which typically has the following structure:



Many cationics are based on polyethylenimine, which is usually of lower molecular weight than polyacrylamide. This is described as a highly branched polyamine produced by the acid catalyzed polymerization of ethylenimine. The polymer is composed of segments which have two carbons per nitrogen randomly distributed in the ratio of one primary nitrogen: two secondary nitrogens: one tertiary nitrogen, as shown below:

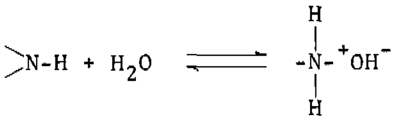


This distribution gives rise to what is believed to be an elipsoid or spheroid shaped molecule composed of many branched segments with the tertiary amino nitrogens being the branching sites and the primary amino nitrogens being the terminal groups of each segment. Thus one segment proposed is as follows, although many others are possible:

$$>N-CH_2CH_2-NH-CH_2CH_2-NH-CH_2CH_2-NH_2$$

The primary and secondary amino nitrogens comprise reaction sites whereby the polymer may be conveniently modified.

In water, the amino nitrogens react with H_2O to form positively charged nitrogens:



$$>N-H + H_2O \rightleftharpoons -\overset{H}{\underset{H}{N}}-{}^{+}OH^{-}$$

From the above reaction it is seen that alkaline solutions are formed. Since the polymer is composed of many nitrogens per molecule there will be many such positive sites - the addition of acid will increase the charge density whereas base will decrease it.

The polymeric structures and scheme of reactions shown above are intended to portray a general idea of the way in which polyelectrolytes are formed. There are many such reactions modifying the final product and producing polyelectrolytes with widely differing properties, that is, with non-ionic, anionic, cationic or ampholytic characteristics, different charge densities and distribution of charge, different molecular weights and so on.

3.2.4.2 Charge Density and Molecular Weight

The effect of charge density, or percentage hydrolysis, of polyelectrolytes is to influence the configuration in solution. For a given molecular weight, increasing charge density has the effect of increasing the viscosity of the polyelectrolyte solution(10). Since viscosity increases with the length of the molecule, the implication is that with increasing charge density, polyelectrolyte chains are increasingly stretched by increasing electrostatic repulsion between charged units. At low charge densities, the polyelectrolyte assumes a tightly coiled almost spherical configuration due to the predominance of Brownian movement; at medium charge density (10 to 20% hydrolysis) the configuration is that of randomly kinked or flexing coils. At high charge densities, the configuration is that of fully extended filamentous rods where the effects of electrostatic repulsion overcome those of molecular bombardment. It is appreciated that, for a given charge density, the longer the polyelectrolyte chain the higher is the viscosity. Hence, it also follows that the higher the molecular weight of the polyelectrolyte, the higher is the viscosity.

Increasing the ionic strength of a polyelectrolyte solution decreases the range of influence of the charged sites on the polyelectrolyte chain (see Chapter 2) and an increasingly coiled configuration is achieved. Concomitantly, the viscosity of the solution decreases.

Charge density and molecular weight of a particular polyelectrolyte both influence the destabilization mechanism and resulting floc formation, the degree depending on the type of polyelectrolyte and the system to which it is applied. This will be discussed further in Chapter 5. As far as molecular weight is concerned, there does not appear to be an upper limit in terms of effective floc formation(11). However, there is a practical limit dictated by the difficulty of dissolving polyelectrolytes with molecular weights in excess of 10^7. The grains of powder swell quickly, but considerable time is required to untangle the long chains. High shear stirring cannot be employed because of breakdown of the polyelectrolyte chains.

3.2.4.3 Dissolution of Synthetic Polyelectrolytes

Synthetic polyelectrolytes are supplied as free flowing bead or granular powders, fine and dusty powders or liquid. The solid types require special dissolution procedures since there is the risk of forming considerable quantities of gelled (*fish-eye*) solids which do not subsequently dissolve.

A common technique for uniformly wetting solid polyelectrolyte particles is to use some form of eductor. As shown in Figure 3.6, the eductor comprises essentially a variable aperture venturi formed between the threaded upper tube and the lower delivery tube. Water entering via the side inlet flows through the venturi producing a vacuum through the powder feed tube, drawing polyelectrolyte into the water stream. The method of operation is to first gently screw the top tube down as far as it will go. Then, with water flowing through the device, slowly unscrew the tube again until maximum suction is obtained as felt by placing a finger over the top of the powder inlet. Normally one to two turns only are required.

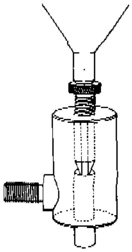


FIGURE 3.6: Eductor for Evenly Wetting Polyelectrolyte Particles Prior to Dissolution. (Courtesy Allied Colloids).

When preparing polyelectrolyte stock solutions in batch mode, the following procedure is normally recommended (refer to Figure 3.7): (i) Run water into the dissolving tank until it is approximately one-third full, and covers the paddle stirrer (or, in the case of Figure 3.7, an air sparger). Note that high speed stirrers are not recommended since, as mentioned earlier, breakup of polyelectrolyte chains may occur; (ii) Commence stirring, turn on water to the eductor, insert *dry* funnel and commence feeding the desired quantity of polyelectrolyte through the funnel; (iii) Continue adding water until a 0,5% solution is obtained; (iv) Continue *slow* stirring for a sufficient ageing period (to allow polyelectrolyte coils to unwind) which depends on the particular product but is usually of the order 1 hour; (v) The prepared solution is passed to a stock solution holding tank; (vi) Dilution water is added downstream of the stock tank and blended with an in-line mixing device (for example, a series of pipe bends).

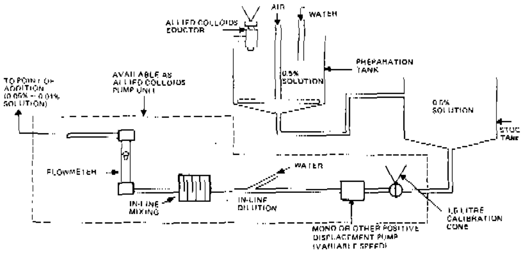


FIGURE 3.7: Batch Polyelectrolyte Dissolution System. (Courtesy Allied Colloids).

Figures 3.8, 3.10 and 3.12 show continuous polyelectrolyte dissolution and feeding systems. The system shown in Figure 3.8 relies on a vibrating device (such as shown in Figure 3.9) to feed a continuous supply of powder to the eductor.

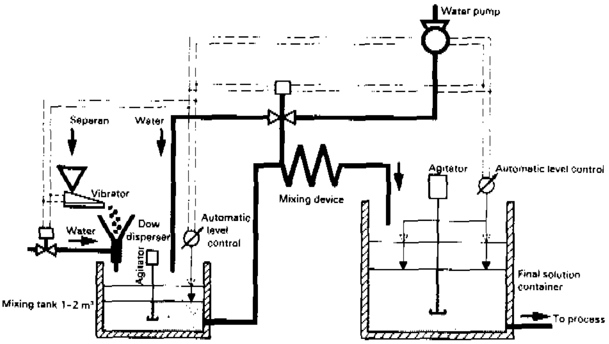


FIGURE 3.8: Continuous Type Polyelectrolyte Dissolution System. (Courtesy Dow Chemicals).

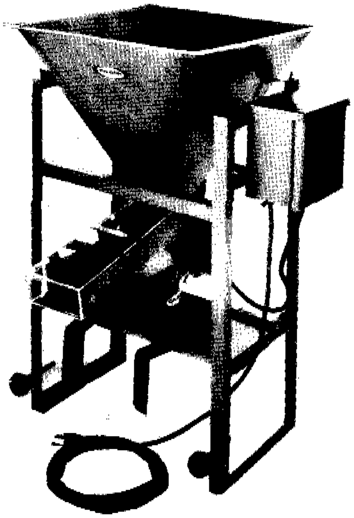


FIGURE 3.9: Example of Volumetric Dry Polyelectrolyte Vibratory Feeder. (Courtesy Calgon Corp.)

Figure 3.10 shows a continuous dissolution system specially designed for bead type solid polyelectrolytes. A dry chemical feeder, b(e.g. screw type, as shown in Figure 3.11) transports solid polyelectrolyte from the bulk container (j) to a hopper (d) and thence to a dry type eductor (e) through which is passed a high velocity air stream from a blower (c). Bead polyelectrolyte is thus passed to dispersers(a) within which an intense water spray pattern ensures uniform wetting of the solid particles. The hose connecting the dry eductor to the disperser is of an antistatic type.

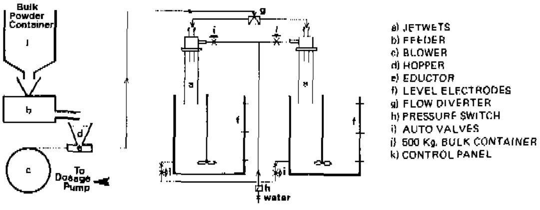


FIGURE 3.10: Example of Bead Type Polyelectrolyte Continuous Dissolution System. (Courtesy Allied Colloids).

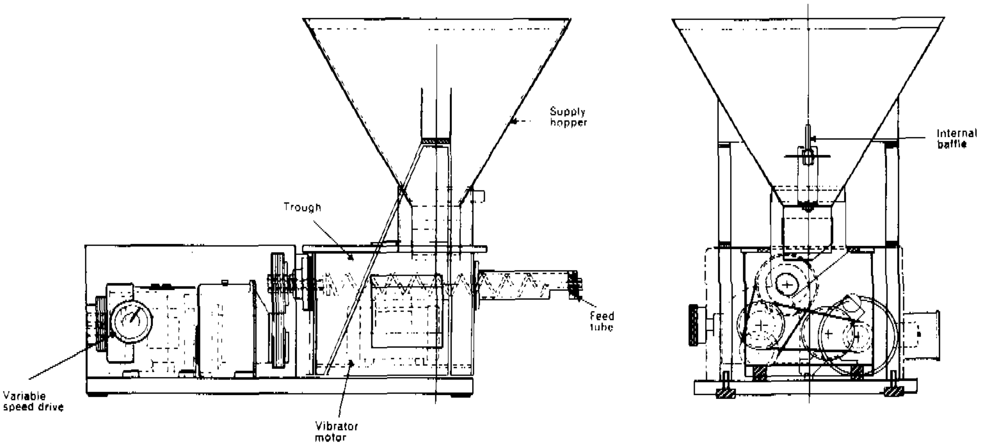


FIGURE 3.11: Example of Screw Type Dry Chemical Metering Feeder. (Courtesy Simon-Barron Ltd.).

In Figure 3.12, polyelectrolyte powder is fed into a disperser from a screw fed dry feeder. A small circular heater is fitted around the feeder outlet to prevent condensation and thus blockages. The disperser provides a high velocity water curtain directed towards the centre. The solid particles, thus wetted are passed into the first of three in-series mixing/ageing chambers to give a total retention time of approximately 1 hour. Diluting water is added downstream of the ageing chambers.

Because of the risk of breaking polyelectrolyte chains both during mixing and during transfer from the stock tank to the point of application, care should be taken in designing feedlines etc. Pumps should not be of the centrifugal type. Mono- or diaphragm types have been used extensively and give good service.

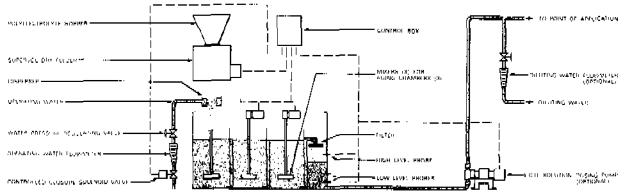


FIGURE 3.12: Example of Continuous Type Dry Polyelectrolyte Product Dissolution System. (Courtesy Wallace and Tiernan Ltd.)

Final dilution of the polyelectrolyte solution should be to a concentration of 0,05 to 0,1%, although this may vary slightly depending on the type of polyelectrolyte. Dosing may be by means of, for example, a variable speed mono (or other positive displacement) pump with calibrated discharge. Flowmeters (e.g. rotameters) may be used with polyelectrolyte solutions at concentrations less than 0,1%. An in-line 0,15 mm mesh filter should be installed to protect the flowmeter from undissolved polyelectrolyte gel particles.

Multipoint addition to the stream to be treated is often recommended by manufacturers. This could be merely a measure to overcome inefficient mixing(16) (see Chapter 6) and local overdosing(8), but it has been suggested(1) that loops formed on adsorption of polyelectrolyte chains - of importance for a *bridging* mechanism of destabilization (see Chapter 5) are retained for longer periods of time. However, there is no conclusive evidence on this point.

3.2.4.4 Toxicity of Synthetic Polyelectrolytes

Although polyelectrolytes such as activated silica, sodium alginate and modified starches may be inferior in effect when compared to some synthetic products, they have the advantage of being virtually completely non-toxic when used for potable water treatment.

With synthetic products, although there is no evidence that polymerised species are of high toxicity(16) the un-polymerised monomer species are. For example, acrylamide is extremely toxic producing severe neurotoxic effects. Packham(16) reports experiments carried out on rats, guinea pigs, rabbits, cats and monkeys where it was demonstrated that ingestion of acrylamide produced progressively stiffness and weakness of hindquarters, loss of ability to control hindquarters, urinary retention, ataxia of the front legs and inability to stand. The 50% lethal dose, LD50 for these animals was of the order 150 to 180 mg.kg d^{-1} on a day to day basis. For humans, it is recommended that total absorption of acrylamide should not exceed 0,005 mg.kg d^{-1}. From this, for a polyacrylamide containing 1% monomer, the concentration to public water supplies that would be required for an 80 kg man drinking 2 l water per day, is 2 mg l^{-1}. This assumes that the acrylamide monomer is not adsorbed by floc particles. However,many commercial polyacrylamides contain considerably less than 1% monomer and most manufactures produce a wide range of special potable water grades where the monomer content is guaranteed at a low figure. Furthermore, in potable water treatment the polyelectrolyte dosage is usually much less than 2 mg l^{-1}.

To safeguard the general public against any likely toxicity by chemical additives to water supplies, the Department of the Environment, U.K. and Environmental Protection Agency, U.S.A., regularly publish lists of approved products, with recommended concentrations. Pertinent information from the current lists (at the time of writing) together with supplementary information, is presented in Appendix A2.

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4

Destabilization with Metal Coagulants

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4.0 INTRODUCTION

A mechanism of destabilization of hydrophobic colloids with indifferent electrolytes has already been discussed in Section 2.7. It was seen that by increasing the ionic strength of the solution, compression of the double layer occurs thereby reducing the range of interparticle repulsion. For a given suspension, as the ionic strength is incrementally increased, the transition from stability to destabilization occurs over a narrow range of electrolyte concentration. Furthermore, if the indifferent electrolyte is increased to excess, there is no effect on destabilization.

Since the effect of an indifferent electrolyte is merely to increase ionic strength, that is, to increase the effective concentration of counter-ions in the vicinity of the charged surfaces without the occurrence of adsorption, the electrolyte (or coagulant) concentration required for destabilization is independent of particle concentration. Furthermore, for the case of indifferent electrolytes, the efficacy of a coagulant is strongly dependent on the valency of the counter-ions such that for mono-, di-and trivalent counter-ions, the concentration of coagulant required would be in the ratio 800:12:1 respectively (see Section 2.7.3).

However, in the majority of cases, the above phenomena may not occur simultaneously and in some cases, not at all. For example, restabilization of a suspension often takes place if an excess of coagulant is applied; the particle concentration often has an effect on the concentration of coagulant required for destabilization (in some cases a stoichiometric relationship is evident) and the efficacy of multivalent coagulant species may be even more so than predicted by the $1/z^6$ Schulze-Hardy rule.

From the above, it is evident that further considerations beyond that of double layer repression by increasing ionic strength are of importance: As stated previously, the latter mechanism does not consider the possibility of adsorption at particle surfaces: As seen in Section 2.4, adsorption of species in solution does occur at the particle surface and may augment the original charge carried by the particle or, in the case of adsorption of counter-ions, may negate or even cause charge reversal. Furthermore, as inferred above, adsorbable coagulant species are observed to destabilize hydrophobic colloids at much lower concentrations than is the case with species of low adsorptivity.

With the acknowledgement of the rôle of adsorption during destabilization with metal coagulants, two further mechanisms may be advanced: the first is described as *adsorption destabilization* which ultimately has a similar effect to that of the *physical double layer* mechanism already described. That is, through adsorption of charged coagulant species of opposite sign to the particle surface, the *effective* surface charge is reduced and as a consequence, the extent of double layer repulsive interaction between adjacent particles is reduced.

The second mechanism considered, again as a result of adsorption of coagulant species at the particle-solution interface, is that described as a *bridging* mechanism. As seen in Section 3.1.2, metal coagulants during hydrolysis reactions have a pronounced tendency to polymerization; As the extent of hydrolysis increases, progressively higher polynuclear species form. On adsorption of such polymeric species to particles a coagulant bridge spanning between adjacent particles is formed thereby promoting destabilization.

It will be seen in Chapter 5 that the above mechanisms are not confined to metal coagulants. Similar considerations apply to destabilization by polyelectrolytes where both bridging and an electrostatic phenomenon are accepted as mechanisms of destabilization.

A further mechanism of destabilization by metal coagulants is that of precipitate enmeshment. As seen in Section 3.1.2.4, under appropriate conditions of coagulant concentration and pH, metal coagulants in aqueous solution form metal-hydroxide precipitates. Such species serve to enmesh particulate material thus effecting destabilization essentially by a *sweep* action. Here, apart from perhaps serving as nuclei for precipitation, the presence of particulate material is incidental.

Precipitation mechanisms are also of importance during destabilization of hydrophilic colloids. Here, because of the extent of hydration, electrostatic effects are relatively unimportant. Coordination reactions occur between metal ions and certain functional groups on the particle surface which serve as ligands. Destabilization is visualized as being the result of metal ion - functional group - hydroxide precipitate formation. Furthermore, with the removal of certain anions from solution (for example phosphorus removal in tertiary wastewater treatment) precipitation reactions occur between metal-ions, anions and hydroxides.

The four mechanisms of destabilization put forward for metal coagulants will be discussed more fully in the following sections (note that a greater in-depth coverage of the bridging mechanism is reserved for Chapter 5, where destabilization mechanisms for polyelectrolytes are dealt with); However, to give a preliminary overall picture of the four mechanisms, Table 4.1 (adapted from Stumm and O'Melia(48)) presents various pertinent characteristics. From these characteristics it is evident that destabilization with metal coagulants cannot be exclusively attributed to any one particular mechanism; In a *particular instance destabilization may be contributed to by* one or several mechanisms.

4.1 DESTABILIZATION OF HYDROPHOBIC COLLOIDS

4.1.1 Extent of Hydrolysis and Adsorption

It was seen in Chapter 3 that metal coagulants during the transition from the *free* aquo metal ion to the insoluble metal hydroxide precipitate, undergo a series of hydrolytic reactions. It is strongly evident that the hydrolysis products of metal coagulants in aqueous solution are adsorbed more readily than free aquo metal ions; The greater the degree of hydrolysis, the more extensive is adsorption. In fact, replacing at least only one coordinated water molecule of the hydrated metal ion by a hydroxyl ion enhances significantly the adsorptivity of the ion(35).

The reasons for the enhanced adsorptivity of hydrolyzed metal ions on hydrophobic colloid surfaces are not understood. Evidently the presence of hydroxyl ions in the coordination sheath is to a large extent responsible but just why hydroxyl ions are able to promote counter-ion adsorption remains to be resolved. As seen in Chapter 2 the electrostatic contribution to counter-ion adsorptivity may be negligible. For this reason adsorption of hydrolyzed neutral species (for example, $Al(OH)_3$) and co-ions does occur, the latter often evidenced by an increase in the original charge carried by the particles. Accepting that the presence of hydroxyl ions does play a part during adsorption, it is appreciated that, as stated before, the greater the degree of hydrolysis (and, concomitantly, the greater the degree of polymerization) the more extensive is adsorption. One can visualize that with extensive hydrolysis, successively higher numbers of hydroxide groups per compound can be adsorbed at the interface.

One may further postulate that the replacement of water molecules by hydroxyl ions in the coordination sphere of a metal ion imparts a certain degree of hydrophobicity to the complex(48); Hydrophobic colloidal particles do not adsorb unhydrolyzed aquo metal ions for the same reason that they do not adsorb water molecules(35). Furthermore, with a dispersion destabilized with hydrolyzed metal coagulants, if the suspension is made sufficiently acidic restabilization occurs as evidenced by reversion of particle surface charge

PARAMETER	INFLUENCE OF INDICATED PARAMETER ACCORDING TO MECHANISM			
	PHYSICAL DOUBLE LAYER	ADSORPTION DESTABILIZATION	BRIDGING	PRECIPITATION
Electrostatic Interactions	Predominant	Important	Subordinate	Subordinate
Chemical Interactions and Adsorption	Absent	Important	Predominant	May occur but not essential for removal
Zeta potential for optimum destabilization	Near zero	Not necessarily zero	Usually not zero	Not necessarily zero
Addition of excess coagulant	No detrimental effect	Restabilization usually accompanied by charge reversal; may be blurred by precipitation	Restabilization due to complete surface coverage	No detrimental effect
Fraction of surface coverage (θ) for optimum floc formation	Negligible	$0 < \theta < 1$ (See Chapter 5)	$0 < \theta < 1$	Unimportant
Relationship between optimum coagulant dosage and particle concentration (for a given suspension)	Optimum dosage virtually independent of colloid concentration	Stoichiometry possible but does not always occur	Stoichiometry between dosage and particle concentration	Optimum dosage virtually independent of colloid concentration
Physical properties of flocs produced	Dense, great shear strength but poor filtrability in cake filtration	Flocs of widely varying shear strength and density	Flocs of 3 dimensional structure; low shear strength, but excellent filtrability in cake filtration	Flocs of widely varying shear strength and density

TABLE 4.1: CHARACTERISTICS OF DESTABILIZATION MECHANISMS WITH METAL COAGULANTS

back to the original value (determined by electrokinetic measurements). Such desorption of metal ion species is due to de-hydrolyzation and a return to the aquo metal ion state. Such a desorption process is slow when compared to the rapidity of adsorption of hydrolyzed species(35). This indicates a slow replacement of complexed hydroxyl ions by water molecules on acidification.

4.1.2 Effect of Coagulant Dosage

As seen in Table 4.1, the effect of coagulant dosage on destabilization depends very much on the destabilization mechanism operative. For example, in certain instances where the mechanism of electrical double layer repression by increasing ionic strength is the predominant mechanism (as is probably the case with synthetic rubber latex particles destabilized with sodium or barium ions(22)) then a destabilization response to coagulant concentration curve of the form shown in Figure 4.1 will probably be obtained. The suspension passes from stability to destabilization over a narrow range of coagulant concentration. The critical coagulant concentration (CCC) is identified as the inflection point on the curve.

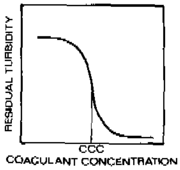


FIGURE 4.1: Destabilization Characteristics Where an Electrical Double Layer Repression Mechanism is Predominant. Increasing the Coagulant (Indifferent Electrolyte) Concentration Beyond the CCC (Critical Coagulant Concentration) Has No Effect.

In such instances, the CCC is independent of particle concentration since destabilization relies solely on the concentration of counter-ions in solution. Furthermore, increasing the coagulant concentration beyond the CCC has no effect; Once the ionic strength is sufficient to compress the diffuse part of the double layer sufficiently for spontaneous destabilization to occur, no further advantage in increasing ionic strength is attained. Moreover, it is in such cases where the Schulze-Hardy $1/z^6$ rule is most likely to be applicable. Consequently, the valency of the counter-ions has a profound effect on destabilization; the higher the valency, the lower is the CCC for destabilization.

Often, from results obtained during destabilization of certain suspensions, more than one destabilization mechanism is evident, depending on the coagulant concentration applied; the concentration of particles in the suspension and the pH.

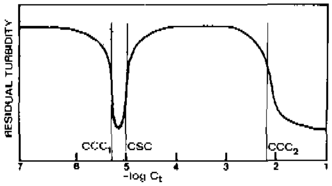


FIGURE 4.2: Destabilization Characteristics Where Adsorption of Coagulant Species to Colloidal Particles is Operative. CCC_1 and CSC Signify The Concentrations, C_t, of Coagulant Necessary to Destabilize and Restabilize Respectively the Dispersion. A Further Critical Coagulant Concentration, CCC_2, Indicates the Occurrence of a Double Layer Repression or Enmeshment Mechanism at Higher Coagulant Dosages. The Data Was Taken from Stumm and O'Melia(48) for Destabilization of a Silica Dispersion (Surface Concentration = = 10 m^2 l^{-1}) With Fe(III) at a pH of 4,0.

Considering for the time being coagulant concentration only, Figure 4.2 (adapted from Stumm and O'Melia(48)) shows results obtained for destabilization of a silica dispersion (surface concentration = $10m^2l^{-1}$) with Fe(III) at a pH of 4,0. It is seen that with increasing coagulant concentration, there are two regions where destabilization is obtained. The first region, identified as CCC_1, occurs when sufficient metal-hydroxide coagulant species are present to become adsorbed and thereby destabilize the suspension. The mechanism here is one of either adsorption of charged metal hydroxide species, giving rise to reduction of charge or charge neutralization; or adsorption of polymerized metal hydrolysis species giving rise to a bridging mechanism of destabilization. The first mechanism is probably predominant at low colloid (surface) concentrations, whereas with relatively higher colloid concentrations, the second (bridging) mechanism may become predominant. A mechanism of destabilization predominantly by diffuse layer compression is discounted because if a higher coagulant dosage is initially applied, restabilization occurs. The initial concentration of coagulant required for restabilization is identified on Figure 4.2 as the CSC (critical stabilization concentration). Restabilization could occur either because of an excess of counterion adsorption giving rise to charge reversal; or excess adsorption of polymeric species occupying too many adsorption sites thereby preventing bridge formation between adjacent particles.

It is seen that by increasing the initial applied coagulant concentration sufficiently, a further destabilization region is evident, the critical coagulant concentration for this region being identified as CCC_2 on Figure 4.2. Again, there are two possible mechanisms, the predominance of each depending on the colloid concentration. At relatively high colloid concentrations, the predominant mechanism is probably due to ionic strength effects. That is, the presence of charged counter ions in solution gives rise to double layer repression. Alternatively, perhaps predominantly at lower colloid concentrations, metal hydroxide precipitates are formed; *Destabilization* in this case arises from a sweep mechanism of colloid enmeshment by precipitates.

It is apparent from the above discussions that besides coagulant concentration, there are at least two other factors influencing the destabilization characteristics of a given suspension of hydrophobic colloids. These are the concentration of colloids in the suspension and the pH existing during destabilization. The following sections deal with each in turn.

4.1.3 Effect of Colloid Concentration

The preceeding section discussed the effect of coagulant dosage on the destabilization of hydrophobic colloids. This section extends the discussion to include the effect of colloid concentration. Figure 4.3 (adapted from Stumm and O'Melia(48)) demonstrates schematically the relationship between coagulant dosage and colloid concentration, the latter in terms of surface area concentration. (Note, the following discussion may be taken as applicable for a pH of approximately 4 to 5). The shaded area indicates zones where destabilization has occurred. The relationships shown in Figure 4.3 are for one particular value of pH; Note that there will be several such diagrams, each at a particular pH value. Four zones are identified as follows:

Zone 1 - indicates that insufficient coagulant has been applied to the colloidal suspension and that destabilization does not take place;

Zone 2 - refers to the region in which destabilization has taken place;

Zone 3 - is that region where destabilization and then, subsequently, restabilization has taken place, due to excessive coagulant addition and

Zone 4 - is the region where the coagulant dosage is high enough to achieve oversaturation, and precipitation of metal hydroxide species occurs.

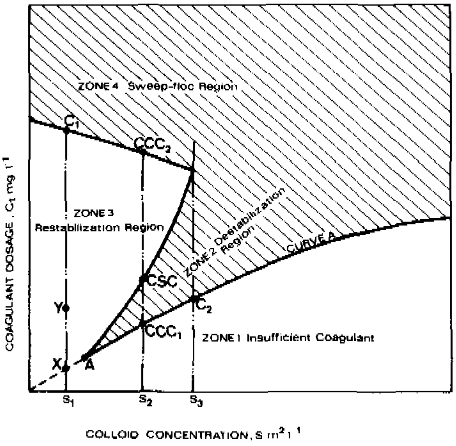


FIGURE 4.3: Zones of Destabilization and Restabilization at a Given pH Value as Related to Colloid Concentration, S, and Coagulant Dosage, C_t. (See Figure 4.2). (Adapted from Stumm and O'Melia(48).

Figure 4.3 is explained as follows: At very low concentrations of colloids (S_1, say) there is very little contact opportunity for colloid-colloid interactions. When a quantity of metal coagulant such as X is introduced, even though the (extrapolated) stoichiometric coagulant dosage may be applied, uneven adsorption occurs and, therefore, a certain number of particles will remain stable, some will suffer charge reversal, some will be destabilized and so on. The problem here, therefore, is visualized as being one of inadequate dispersion.

Suppose an increased coagulant dosage, Y, had been applied. The situation now exists where, although colloids are still greatly dispersed, there is an ample supply of coagulant species for each colloid. However, the concentration of coagulant with respect to the colloid concentration is relatively high so that excessive adsorption takes place and restabilization occurs as described in Section 4.1.2. The only way in which it is possible to remove the colloidal solids is to increase the coagulant concentration to a value of at least that given by C_1. Here metal hydroxide precipitates form and removal is by a sweep mechanism.

It is seen that at colloid concentrations such as S_1, increasing colloid concentration concomitantly results in a decreased coagulant concentration, until at a concentration corresponding to point A on the diagram, there is a precipitous decrease in the coagulant dosage required for destabilization. This may be explained in terms of contact opportunity between coagulant species and colloids. As the colloid concentration progressively increases, adsorption of transition hydrolysis products occurs to a certain extent thereby forming nucleic sites for precipitation. In this way, less coagulant is progressively required to form precipitates. At a certain colloid concentration (such as that corresponding to point A) contact opportunity is sufficient for hydrolysis species to become adsorbed and effect destabilization by charge effects or bridging, before precipitation takes place. With kaolin clay suspensions, point A probably corresponds to a suspended solids concentration of the order 50 to 100 mg l^{-1} (based on kaolinite)(28, 38, 40).

Referring to Figure 4.3 it is seen that waters of low solids concentration may be more efficiently destabilized by augmenting the total surface area to a value such as that given by S_2,for example. This is carried out in some cases of water treatment practice where bentonite or activated silica may be added.

At colloid concentrations such as S_2, it is seen that the critical coagulant concentration for destabilization is much less than for S_1. However, destabilization occurs over a relatively narrow range of coagulant dosage. Beyond a critical dosage (CSC) restabilization of the suspension occurs. Significant colloid removal for coagulant dosages greater than CSC only occurs when a quantity of coagulant sufficient for precipitation is added. As discussed in the preceeding section, the mechanism of destabilization for coagulant dosages between the CCC and CSC is one dependent on adsorption. Because of the predominance of an adsorption type mechanism in this region of colloid concentration, one would expect a dependence of the critical coagulant concentration on colloid concentration. This is seen to be so by a consideration of the linearity of curve A in this region. Such stoichiometry probably occurs when suspended solids concentrations are greater than that represented by point A, that is, of the order 50-100 mg l^{-1} (based on kaolinite).

At high colloid concentrations (S_3 and higher) it is seen that restabilization does not occur. This may be explained by considering chronologically the action of metal hydrolysis species in solution: The first effect must be compression of the diffuse part of the double layer, rather than extensive adsorption; As stated earlier, adsorption is more favourable with the higher metal-hydroxide species. Hence, before extensive adsorption takes place with its eventual related charge reversal, colloids, being in closer proximity than the preceding cases considered, will be destabilized and will have already formed flocs. Hence the region corresponding to colloid concentrations in excess of S_3 does not imply a sweep floc region, but rather a region of destabilization brought about by a double layer repression mechanism. This is supported by the shape of line A which is horizontally asymptotic with increasing colloid concentration; For a physical double layer mechanism, colloid concentration has no effect on the coagulant dosage for destabilization. It should be noted, however, that if the coagulant dosage is very high, then metal-hydroxide precipitates will form, but there would appear to be little advantage from the point of view of destabilization efficiency.

Hence, summarizing the above: for low colloid concentrations, less than that corresponding to point A, the destabilization mechanism is one governed by precipitate formation. For medium concentrations, between A and S_3, the destabilization mechanism is governed by adsorption and charge reversal may occur. Here, a model of the form proposed by Stern (see Chapter 2) would adequately describe the phenomena. For high colloid concentrations (greater than S_3) a double layer mechanism, such as that described by the Gouy-Chapman model, is probably predominant. For medium and high colloid concentrations, destabilization may be brought about by high coagulant dosages where metal-hydroxide precipitates are induced to form.

4.1.4 Effect of pH

4.1.4.1 General

The discussion in Section 4.1.3 was directed towards the combined influence of colloid concentration and coagulant dosage on the characteristics of destabilization of hydrophobic colloids. A further factor, of paramount importance in destabilization with hydrolyzing metal coagulants, is the pH. As seen in Chapter 3, the predominance of a particular hydrolysis species during destabilization is very largely dependent on the pH value. For a particular colloidal suspension, it is logical to consider that there exists a particular hydrolysis species most effective for destabilization; whether by virtue of the charge carried; or adsorptivity and so on. To quote Black and Chen(9): *The adjustment of pH to a range where the most effective hydrolysis species of the coagulant is formed is shown to be very essential in producing optimum coagulation.*

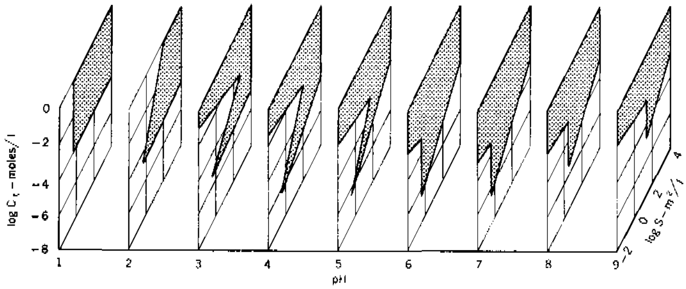


FIGURE 4.4: Zones of Destabilization and Restabilization as Related to pH, Colloid Concentration, S and Coagulant Dosage, C_t. (See Figures 4.2 and 4.3). {From Stumm and O'Melia(48), With Permission of The American Water Works Association}

Figure 4.4(48) shows the interrelationship between coagulant dosage, solids concentration and pH for the particular case of a silica dispersion using Fe(III) as coagulant. It is seen that at each pH value, curves of a similar form to that of Figure 4.3 are obtained. It is instructive to study each pH value in turn:

4.1.4.2 pH 1,0

From Figure 4.4 it is seen that at low colloid surface concentrations appreciable destabilization does not occur. Furthermore, it is seen that the coagulant concentration for destabilization is independent of colloid concentration and restabilization does not occur. This may be explained by a consideration of the probable hydrolysis species existing at this pH value. From Figure 3.5(a) it is seen that hydrated aquo metal ions are predominant. Therefore, it follows from the above observations that the mechanism of destabilization is almost totally due to double layer repression by ionic strength considerations. The absence of destabilization at low colloid concentrations can be explained in terms of kinetic effects where contact opportunities are too low for appreciable perikinetic flocculation in the time allowed for destabilization.

4.1.4.3 pH 2,0

Here, it is seen that similar characteristics to that at pH 1,0 are evident; with one important exception: at low to medium colloid concentrations restabilization occurs. Referring to Figure 3,5(a) (for, say, a total Fe concentration of 10^{-3}M) it is apparent that hydrolysis products begin to have significance at pH 2,0. As stated previously, hydrolysed metal coagulant species have a pronounced tendency for adsorption. At pH 2,0, therefore, destabilization is significantly influenced by adsorption such that excessive dosages lead to surface charge reversal and restabilization.

At high colloid concentrations, destabilization is due to double layer repression by positively charged transition coagulant species.

4.1.4.4 pH 3,0 to 5,0

From the destabilization curves for pH 3,0 to 5,0, it is seen that at a given pH the coagulant dosage - colloid concentration relationship is as discussed in Section 4.1.3. To briefly recapitulate: for colloid (surface) concentrations greater than approximately 1,0 $m^2 l^{-1}$ (for the colloid system considered here) the destabilization mechanism is one of adsorption; as evidenced by the dependence of coagulant dosage for destabilization on colloid concentration (lower boundary of the destabilization zone) and the occurrence of restabilization. The upper destabilization zone is one of metal-hydroxide precipitate enmeshment. At higher colloid concentrations the mechanism is increasingly one of double layer repression.

From Figure 4.4, it is seen that the slope of the critical coagulant dosage-colloid concentration boundary increases with increasing pH. This indicates an increasing dependence of the destabilization mechanism on adsorption; referring to Figure 3.5(a) it is seen that within the range of critical coagulant dosage ($\pm$ 10^{-5} M), at pH 3,0 7% of coagulant species are hydrolyzed and at pH 5, full hydrolysis is apparent.

Restabilization at each pH value is also explained by increasing hydrolysis. For example, at a pH of 3,0 the percentage hydrolysis of coagulant species at the critical dosage for destabilization is approximately 7%. Increasing the dosage to 10^{-4} M (approximately corresponding to the CSC) the percentage hydrolysis is 60%. Hence, increasing dosage in each case gives rise to increased hydrolysis and consequently increased adsorption. At low pH values (pH 3,0) the predominant species are positively charged: hence, restabilization is due primarily to charge reversal. At higher pH (5,0) the predominant species are negative (for example, $Fe(OH)_4^-$) and one may postulate a mechanism of bridging with excessive surface site coverage resulting in restabilization.

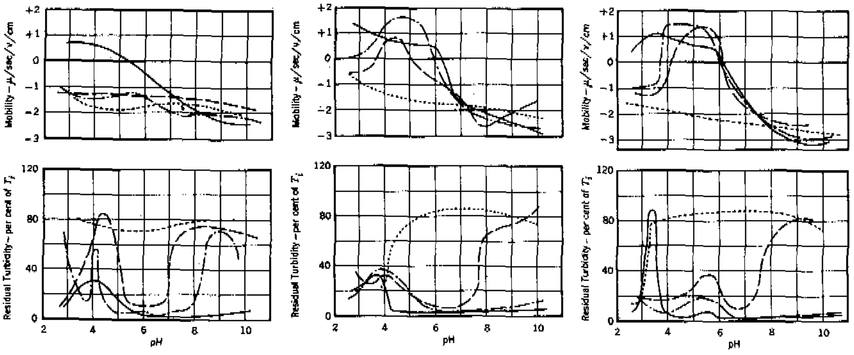
4.1.4.5 pH 6,0 to 9,0

For pH values of 6 and higher, it is seen that restabilization does not occur. This may be explained by a destabilization mechanism of bridging by negative hydrolysis species with a continuous transition to precipitate enmeshment as the dosage is incrementally increased. The progressively increasing dosage for destabilization with increasing pH supports the predominance of negative hydrolysis species since with increasing negativity statistically less contact opportunity is afforded between coagulant species and colloidal particles.

Evidence for the increasing predominance of negative hydrolysis species would be provided if electrophoretic mobilities on coagulant addition were to become increasingly negative with increasing pH. This is seen to be so from Figure 4.5(8) which shows (a) ferric sulphate added to destabilize a montmorillonite suspension; (b) a fuller's earth suspension and (c) a kaolinite suspension. In general, initially (at low pH values) the mobility values are seen to increase to positive values (which follows from the discussions above where positive hydrolysis species were postulated); at higher pH values the mobilities are seen to increase in negativity.

4.1.4.6 Further Considerations

Although the above sections considered the particular case of destabilization of hydrophobic colloids with iron coagulants, the same reasoning applies to other systems. For example, Black and Chen(10) found that with aluminium sulphate applied to kaolinite suspensions, destabilization at pH 3,0 was due to electrical double layer depression by unhydrolysed $Al(H_2O)_6^{3+}$. At pH 5,0, destabilization was due to adsorption of positively charged polynuclear aluminium hydrolysis products with restabilization occurring after a narrow range of coagulant dosage due to charge reversal. The optimum dosage for destabilization was 5 mg l^{-1} which corresponds to anAl(III) concentration of $1,5.10^{-5}$ M. Referring to the work of Singley <u>et al</u> (see Section 3.1.2.4) it is seen that this is the order of concentration where complicated, polynuclear hydrolysis products form, such as those shown in Figure 3.4(b). With such highly charged strongly adsorptive species the occurrence of restabilization is self apparent.



a. Comparison of the Effects of pH and Mobility on Coagulation of Montmorillonite Suspensions With Ferric Sulfate

b. Comparison of the Effects of pH and Mobility on the Coagulation of Fuller's Earth Suspensions With Ferric Sulfate

c. Comparison of the Effect of pH and Mobility on the Coagulation of Kaolinite Suspensions With Ferric Sulfate

FIGURE 4.5: Evidence for the Increasing Predominance of Negative Hydrolysis Species With Increasing pH: At *Higher pH values Mobilities Increase in Negativity.* T_i Represents Initial Turbidity. The Dotted Curves are for No Ferric Sulphate Added; The Dashed Curves for 3ppm Ferric Sulphate; The Dot-Dash Curves for 5ppm and the Solid Curves for 50ppm. (From Black and Walters(8), with permission of the American Water Works Association).

At pH 8,0 the destabilization mechanism with increasing coagulant dosage is a gradual transition from adsorption of positively charged hydrolysis species to precipitate enmeshment with $Al(OH)_3$ species.

In this and preceding sections, although a logical account has been attempted of the phenomena occurring during destabilization of hydrophobic colloids with metal coagulants, there are certain instances where explanations are not so readily forthcoming. For example, Black and Chen(9) during investigations on destabilization of various clay suspensions with aluminium sulphate, found that a region of high turbidity removal was consistently obtained at pH values of 10,0 and above.

The predominance of negatively charged hydrolysis species at such pH values (see Figures 3.5a and b) especially at lower coagulant dosages would suggest an adsorption bridging type mechanism. However, this was not reflected in the electrophoretic mobility values obtained by Black and Chen which remained relatively constant with increasing pH at pH values greater than about 8,0.

Mackrle(30) has suggested the influence of hydrous-oxide crystals at higher pH values of the form $nAl_2O_3.H_2O$ and $nFe_2O_3H_2O$. A possible explanation of the results described above may be a combined effect of, for example, negatively charged $Al(OH)^{4-}$ and positively charged Al_2O_3 species.

4.2 DESTABILIZATION OF HYDROPHILIC COLLOIDS

4.2.1 General

Hydrophilic colloids, because of hydrated layers surrounding them, are not destabilized by such considerations as depression of the electrical double layer. However, hydrophilic colloids do carry a surface charge although the effective range of influence may be confined in some cases to within the hydrated layer.

The surface charge carried by hydrophilic colloids is often due to the ionization of ionogenic groups. Such groups may be carboxylic; aliphatic or aromatic hydroxyl, sulphato, phosphato and aminogroups. Stumm and Morgan(47) by means of alkalimetric titration curves demonstrated that metal ions form complexes readily with ligands such as phosphates, pyrophosphates, salicylates (which contain a carboxyl and an aromatic hydroxyl group) and oxalates. Such ligands are representative of the functional groups of many hydrophilic colloids.

The above substances, as ligands, do not have as great an affinity with metal ions as do OH^- ions. However, statistical considerations play a significant rôle in selective coordination and the preference of, say, phosphates over OH^- will depend on the ratio $\{phosphate\}/\{OH^-\}$. Phosphates will, therefore, tend to be preferentially coordinated at lower pH values. This reasoning also applies to other ligands. Furthermore, to form an electroneutral precipitate, less OH^- ions will be required in the coordination sphere of the metal-ion complex so that the pH for precipitation will be lower in the presence of such ligands than if OH^- were the only ligand present.

Stumm and Morgan considered the destabilization of hydrophilic colloids carrying functional groups such as those described above, to be principally due to precipitation of the metal-ligand complexes. This is substantiated by two facts: a) it is known that destabilization of hydrophilic colloids does take place at acidic pH values, which tends to indicate preferential co-ordinative reactions with metal ions and functional groups at the colloid surfaces and b), it is further known that to destabilize a dispersion of hydrophilic colloids requires higher coagulant dosages than their hydrophobic counterparts. This suggests that the system will be oversaturated with respect to the metal ion-ligand complexes which results in precipitation.

In the following sections two specific groups of hydrophilic colloids will be discussed, although the principles involved are applicable to a certain degree to hydrophiles in general. The first concerns removal of humic substances and the second viruses.

4.2.2 Organic Colour Removal With Metal Coagulants

4.2.2.1 General

Although organic colour is included here in a section dealing with hydrophilic colloids, it is debatable whether colour is colloidal or in true solution. Shapiro

(42) suggested that colour compounds were straight-chain-substituted fatty acids in true solution and that colloidal properties exhibited by these compounds are due to complex formation with iron if present in solution. It has been suggested(39) that of the humic fractions present in organic coloured waters, the humic acid fraction is colloidal whereas the fulvic fraction is in true solution. Black and Christman(5) by filtration and electrophoretic measurements concluded that organic colour causing compounds were true hydrophilic colloids possessing a negative surface charge. They further suggest that colour is due to a light scattering and fluorescence effect rather than to molecular absorption. Packham(39) has suggested that organic colour is in true solution but that a proportion of the molecules are large enough to exhibit colloidal properties. Furthermore, in the presence of iron coordination reactions may occur giving rise to colloidal characteristics.

However, although it cannot be categorically stated whether organic colour is colloidal or in solution, the material does exhibit hydrophilic colloidal properties such that the apparent destabilization mechanism can be conveniently included with that of hydrophilic colloids.

4.2.2.2 Nature of Organic Colour

Organic colour is usually associated with soft surface waters containing little or no alkalinity. It arises from the aqueous extraction of living woody substances, the solution of degradation products in decaying wood, the solution of soil organic matter or a combination of these. Christman and Ghassemi(15) suggested that the manifestation of colour is an intermediate step in the transformation of organic matter from living or decaying woody tissue to the soil organic complex.

Humic substances include a wide variety of compounds with similar constitution and properties. Odén(37) classified humic substances in terms of four fractions, as shown in table 4.2 (Odén's original terminology has since been modified).

TABLE 4.2

GROUP NAME	ALTERNATIVE NAMES	DEFINITION
Humus coal	Humin, ulmin	Insoluble in water and sodium hydroxide
Fulvic acid	Crenic and apocrenic acids	Soluble in sodium hydroxide and mineral acid
Hymatomelanic acid	Hæmatomelanic, hematomelanic, ulmic acids	Soluble in sodium hydroxide and alcohol. Insoluble in mineral acid
Humic acid	—	Soluble in sodium hydroxide. Insoluble in mineral acid and alcohol

In natural waters, the predominant fractions present are fulvic, hymatomelanic and humic acids. The proportions of these fractions are typically in the approximate ratio 10:2,5:1 respectively(5,39). However, variations in the proportions of the fractions do exist. For example, Packham(39) investigating several waters in the U.K., found an average fulvic fraction of 76,4% with a standard deviation of 10,8%; an average hymatomelanic fraction of 16,6% with a standard deviation of 7,7% and an average humic fraction of 7,0% with a standard deviation of 4,6%.

Humic substances derived from a number of sources, although as stated above exhibiting similar properties, are nevertheless usually different from one water to another. Although chemical and spectral properties may be similar, other differences due to physical properties, molecular weight, particle size and so on may give rise to different requirements for treatment.

Packham(39) suggested that differences in properties of humic substances of different waters was due principally to differences in the proportions of the various fractions; each fraction having different properties.

Humic acids possess the highest molecular weights of the three groups, with values of up to 50 000. Hymatomelanic acids are regarded as intermediates between fulvic and humic acids with molecular weights of the order 800(39). Fulvic acids probably have the lowest molecular weights in the groups. Besides being the predominant fraction of coloured waters, fulvic acids, on a unit weight basis, exhibit a higher capacity for colour production than either the hymatomelanic or humic acid fractions(6). It is evident, therefore, that the fraction of major concern in coloured waters is fulvic acid. Some workers(24) suggest that fulvic acids represent a more complex mixture of substances than humic acid, whereas others(41) suggest that fulvic acids are essentially small sized humic acid molecules. Black and Christman(6), found from solubility relationships, chemical spot tests and infrared absorption spectra, indications that fulvic acids are aromatic polyhydroxy methoxy carboxylic acids. These workers suggest that ionization of carboxyl and aromatic hydroxyl groups are responsible for the negative charge of colour compounds.

It is likely that, although the general structure of fulvic acids probably follows that suggested by Black and Christman above, no two molecules of colour compounds are exactly identical; perhaps an indication of this is the variety of structures proposed by several workers(41).

For the purposes of the present discussion, it will be accepted that organic colour is due to negatively charged hydrophilic compounds of colloidal size possessing carboxyl and aromatic hydroxyl functional groups.

4.2.2.3 Disadvantages of Organic Colour in Water Supplies

The presence of organic colour in water supplies is considered undesirable for a number of reasons (16, 17): (a) on aesthetic grounds, consumers prefer a clear colourless supply; (b) humic substances may impart taste to the water, although not necessarily unpleasant; (c) the presence of organic colour increases the disinfection (chlorine, ozone etc.) demand; (d) humic substances have a nutrient effect on microorganisms; (e) many industries require a low colour level, for example, the pulp and paper industry for the production of high brightness bleached paper require a maximum concentration of 5 units or less(4); (f) humic substances may foul ion exchange resins; (g) the presence of colour interferes with water analyses - particularly those based on colorimetry; (h) high colour may reduce the productivity of a water by limiting transmission of light for photosynthesis; (i) humic substances combine with iron, manganese and lead by peptization or chelation, forming *humus metal* complexes(49); (j) besides increasing chlorine demand as mentioned in (c) above, fulvic acids react with chlorine to form potentially carcinogenic haloforms as by products(41).

The above undesirable properties notwithstanding, there is no evidence that humic substances are directly harmful to higher organisms. In fact, although no systematic studies appear to have been carried out, a certain therapeutic value has been claimed with regard to rheumatic fever and certain skin defects(16).

The apparent nutrient effect of humic substances may in some cases be advantageous. The stimulating effect of humics on algal growth has been demonstrated by several workers (16) and may be due to trace metal stabilization by the humics.

4.2.2.4 Measurement of Colour

Because of the complexity of humic substances, it has been necessary to adopt an arbitrary standard for the measurement of colour. The standard accepted is based on platinum-cobalt solutions which produce a yellowish-brown colour similar to that of humic substances. Often a number of colour standards are prepared in Nessler tubes and coloured samples compared visually. However, this method has the disadvantage of subjectivity. At the low colour values of many natural waters, visual comparison is almost impossible; less than 3 Pt-Co units being virtually unnoticeable. An alternative is to calibrate spectrophotometer readings with standard platinum-cobalt standards and take sample colour readings directly with the spectrophotometer. Operation in the UV range (approximately 300 nm) is probably the most appropriate. Adapted spectrophotometer instruments are available(23) that give direct Pt-Co colour readings.

The presence of turbidity in water samples may give rise to an enhanced (*apparent*) colour reading. For a *true* colour measurement, it is recommended(23) that samples be passed through a 0,45 μ membrane filter prior to colour measurement. Removal of true colour causing compounds by filtration is probably negligible.

A difficulty in having a consistent standard of colour measurement is that the colour intensity of a given water varies with pH. Black and Christman(5) found a concurrent pH effect on both the particle size and number of colour producing particles; increasing pH effecting both a decrease in particle size and an increase in particle numbers. Assuming colour to be due primarily to light scattering and fluorescence, as mentioned previously, raising the pH of a given water should increase the colour intensity. As shown in Figure 4.6(46) this is seen to be so. It is further evident that this *indicator* effect is more prominent the higher the initial colour value. For colour values less than 50 Pt-Co units, the indicator effect is negligible.

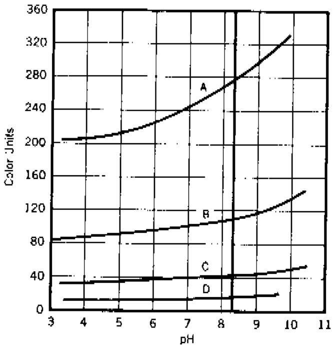


FIGURE 4.6: Effect of pH on Colour of Four Representative Waters. (From Singley et al(46), with permission of the American Water Works Association).

Singley et al(46) suggested reducing all colour measurements to a standard value of pH. A value of 8,3 was chosen because this represents the final pH of most treated waters. For convenience, they present the nomograph reproduced in Figure 4.7. Thereby, a reading of colour for a given water, at any particular pH (from 2 to 10) is readily converted to a standard reading at pH 8,3. As seen on the nomograph, colour values less than 50 units have not been included since, as stated above, the indicator effect is negligible at low values. As noted by Singley et al use of the nomograph is more convenient than adjusting the pH of colour samples, particularly in view of the fact that most coloured waters are low buffered, which results in difficulties of adjusting pH to an exact value.

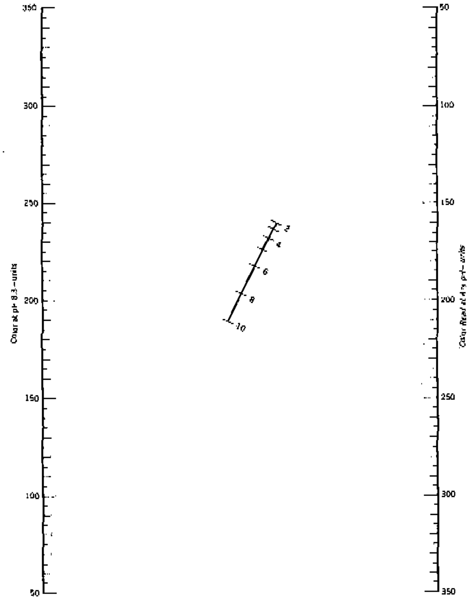


FIGURE 4.7: Colour Conversion Nomograph for Natural Coloured Waters: The Scale at the Centre is for pH at Which Colour Was Read. To Use the Nomograph: (i) Read Colour of Water at any pH; (ii) Place Straight Edge Through Colour Read on Right Hand Scale and pH at Which Colour was Read on Centre Scale and (iii) Read Corrected Colour on Left Hand Side. (From Singley et al(46), with permission of the American Water Works Association).

4.2.2.5 Destabilization of Organic Colour With Metal Coagulants

The mechanism of destabilization of humic substances with metal coagulants is assumed to be that previously described as general for hydrophilic colloids(47). That is, a precipitation mechanism between metal ion and functional groups on hydrophilic colour particles forming multi-ligand complexes together with OH^- and H_2O species. Such a mechanism explains the stoichiometric relationship between metal coagulant dosage and colour intensity, and the lower pH for destabilization when compared with that for turbidity removal. Hall and Packham(24) suggest such a chemical interaction involving metal hydrolysis species such as $Al_n(OH)_{2,5n}$ and probably carboxyl groups on the colour particles. Such an interaction would further explain the near zero zeta potentials at optimum destabilization (4).

The stoichiometry between raw water colour and optimum coagulant dosage has been reported by several workers(7,24) for both aluminium sulphate and ferric salts. In general, the optimum coagulant concentration for fulvic acid is higher than for humic acid at the same concentration(24) indicating that two waters, even though possessing similar colour intensities, may require different coagulant dosages.

Ferric salts, in general, have been found to yield slightly lower colour residuals after destabilization (7,24). However, the optimum dosage for lowest residual colour in each case appears to be the same if concentrations are expressed in terms of the metal ion. The mechanism of destabilization for the different coagulants, therefore, is evidently the same.

Although the optimum dosage - colour relationship with ferric and aluminium salts is essentially the same, the optimum pH values for these coagulants are different: with ferric salts the optimum pH is typically within the range 3,7 to 4,2(7, 24, 31) and with aluminium sulphate within the range 5,0 to 5,5(7, 24). Hall and Packham(24) suggest the differences are due to the greater affinity of ferric ions for OH^-. From the discussions in

Section 4.2.1 it is seen that in this case, for functional groups to serve as ligands in the metal complex, lower pH values are required thereby limiting the statistical opportunity for OH^- ions to be complexed. Furthermore, the lower residual humic concentrations attained with iron indicates that the humic-iron bond is stronger than the humic- aluminium bond(24).

For a given coloured water, Black et al(7) showed that, at the optimum coagulant dosage (specifically ferric sulphate in their experiments) there is a relationship between initial raw water colour and optimum pH, such that for colour values ranging from 50 to 450, the optimum pH varied from 3,8 to 3,45. With the coagulant dosage - colour stoichiometric relationship mentioned previously, it is seen that control of treatment of a given coloured water is greatly facilitated: optimum dosage and pH with changes in colour intensity of the water may be determined from pre-calibrated colour-dosage-pH curves; all colour measurements being carried out or reduced to the standard pH of 8,3 as described in Section 4.2.2.4. However, such a procedure would still require confirmatory routine jar test experiments.

The presence of turbidity in a coloured raw water may complicate treatment, since the mechanisms of removal are probably completely different. Usually, the presence of clay has little effect on colour removal (that is, if optimum conditions for destabilization of such a mixed water are assessed in terms of colour only). However, the presence of colour has an effect very similar to that of the presence of anions such as phosphates on clay turbidity. That is, the optimum pH for destabilization of clay dispersions is progressively shifted to the acid side with increasing phosphate(or colour) concentration. This phenomenon is described in greater detail in Section 4.3.

4.2.3 Virus Removal With Metal Coagulants

4.2.3.1 General

It is pointed out in the World Health Organization International Standards for Drinking Water that treated water, although free of faecal coliforms, may nevertheless transmit viral diseases(21). The most notable waterborne viral diseases are poliomyelitis and type A viral hepatitis, although there are more than 100 different virus types that are excreted with human faeces(50). The percentage of cases of virus infection which are directly attributable to drinking water is not conclusively known since many cases are not notifiable and, furthermore, in many notified cases the source of infection is not determined. However, it has been suggested(36) that of the order 30% of infected cases could be attributed to the water route.

The survival time of viruses in water varies widely and is dependent on the specific virus, temperature and general quality of the water. Under certain conditions and with certain virus types, survival times may be up to 200 days in river water(18).

It has often been reported that chlorine is not wholly effective in virus inactivation(43, 50). A possible reason is that in cases where positive virus counts were obtained in treated waters, insufficient disinfection contact time was allowed. For example, some virus types (Polio 2) require a chlorine contact time of 40 minutes for 99,99 per cent inactivation in the presence of 0,5 mg l^{-1} free chlorine(18). The average contact time (for twenty human viruses(18)) is of the order 15 minutes with the least resistant virus type requiring 2,7 minutes and the most resistant 40 minutes.

Several workers(14, 32, 43, 50) have reported the removals obtained using metal coagulants and/or polyelectrolytes. With metal coagulants, removals of up to 99,9% have been reported for both aluminium and ferric salts. Various polyelectrolytes (cationic) have effected removals of greater than 99% but have the disadvantage that if other material is present in the form of colour, turbidity, COD and so on, removal of such material is poor. Using metal coagulants and polyelectrolytes conjointly has the advantage that better floc characteristics are produced and, furthermore, if a variety of substances are present in water, it is possible that the use of both metal coagulants and polyelectrolytes will effect a higher overall removal. However, this very much depends on the conditions pertaining for each case;

Some workers(43) report that using polyelectrolytes as flocculant aids, although improving floc formation, does not improve virus removals beyond those achieved using metal coagulants alone.

4.2.3.2 *Mechanism of Virus Destabilization With Metal Coagulants*

Viruses are essentially DNA (Deoxyribonucleic acid) or RNA (ribonucleic acid) units contained within a protein coat. The destabilization mechanism involves coordination reactions between metal coagulant species and carboxyl groups of the virus coat protein(14) - in much the same fashion as discussed previously for organic colour compounds. From the similarity of the destabilization mechanisms for organic colour and viruses, one would expect similar conditions of pH at optimum removal. From reported results this is apparently so: for example, Chaudhuri and Engelbrecht(14) report the optimum pH for virus removal with aluminium sulphate to be in the region of 5,0. Percentage virus removals with aluminium sulphate were in the range 97,7 to 99,8%. Turbidity removals were in the range 98,3 to 99,3%. Using a cationic polyelectrolyte as flocculant aid, virus and turbidity removals were increased to 99,9 and 98,5% respectively.

Manwaring et al(32) applied ferric chloride to remove a bacterial virus (bacteriophage MS2 against E. Coli). With an initial virus concentration of $3,9.10^5$pfu (plaque forming units) ml^{-1}, removals of up to 99,7% at a ferric chloride dosage of 60 mg l^{-1} and pH 5,0 were achieved (note that pH 5,0 was the lowest pH studied; perhaps the optimum pH has a lower value than 5,0).

It should be noted that applying metal coagulants or polyelectrolytes does not inactivate viruses(32). Therefore, a potential health hazard exists with disposal of water treatment plant sludges; whether on land or in such a fashion that contamination of surface or ground waters results. Furthermore, complete virus removal by destabilization with metal coagulants has not been reported. For full removal, other methods are required. These include superchlorination, ozonization, sterilization by ultraviolet rays or by ionizing radiation. It has been suggested(21) that from an economic point of view, if an effective vaccine against viral hepatitis were also to be developed, widespread immunization against poliomyelitis <u>and</u> viral hepatitis would be a more economical procedure than improving the treatment of potable water to control water-borne viral diseases.

4.3 EFFECT OF ANIONS

4.3.1 General

In Section 4.2.1 it was mentioned that certain anions tend to displace hydroxyl ions from the coordination sphere of metal ions and that this displacement preferentially occurs at lower pH values. The effect of a particular anionic species on the destabilization characteristics of metal ions applied to a given suspension depends on a number of factors. Marion and Thomas(33) put forward the following general rules: (a) If the anion is a strong coordinator with aluminium and not readily replaced by hydroxyl ions, the pH of optimum destabilization will drop sharply with increasing anion concentration; (b) If the anion is a strong coordinator with aluminium but can be displaced by hydroxide ion, the pH of optimum precipitation increases with a very basic anion, and decreases with a weakly basic anion; (c) If the anion is only a very weak coordinator with aluminium, it exerts only a slight effect on optimum precipitation, generally in the direction of lower pH values.

From the above, nitrates and perchlorates have very little tendency to coordinate with metal ions and, therefore, do not have a notable influence on destabilization with metal coagulants. Chlorides, probably having a weak coordinating capacity with metal ions, shift the optimum pH slightly to the acid side if the concentration is high enough. That is, if the $\{Cl^-\}/\{OH^-\}$ ratio is high enough, hydroxyl ions are displaced from the coordination sphere of metal ion complexes by chloride ions.

With sulphate anions the effect is to <u>extend</u> the pH zone of destabilization towards the acid side whereas with phosphate anions the effect is to <u>shift</u> the optimum pH zone to the acid side. These two cases will be discussed in greater detail in the following sections. Furthermore, the special case of phosphorus removal during tertiary wastewater treatment will be discussed in a separate section.

4.3.2 Effect of Sulphate

With sulphate anions, being relatively strongly coordinated with metal ions and weakly basic, the effect is to broaden the pH zone of optimum destabilization to the acid side(25). This is apparent in Figure 4,8(3) where, with increasing SO_4^{2-} concentration, the pH zone for optimum destabilization is increasingly spread further towards the acid side (in Figure 4,8 the efficiency of destabilization is expressed in terms of the time for floc formation). With increasing sulphate concentration progressively greater opportunity is afforded for mixed ligand complexes to form. This is even more pronounced at lower pH values where the opportunity for SO_4^{2-} to be complexed is further increased.

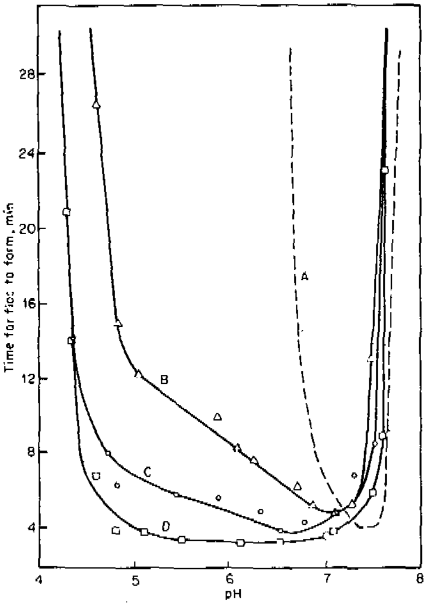


FIGURE 4.8: Effect of Sulphate Ion on Time of Formation of Alum Floc. Broadening of the pH Zone of Coagulation by Sulphate Ion. Curve A, Alum (35 mg l^{-1}) and Sodium Hydroxide; Curve B, Addition of 25 mg l^{-1} SO_4; Curve C, addition of 50 mg l^{-1} SO_4; Curve D, Addition of 125 mg l^{-1} SO_4. (From Black et al(3), with the permission of the American Chemical Society.

Matijević(35) reported the probable predominance of tetrapositively charged mixed ligand complexes of the form $\{Al_8(OH)_{10}(SO_4)_5\}^{4+}$ at pH values in the region 4,5 to 7,0 for aluminium sulphate applied to destabilization of silver halide sols. At lower pH values relatively ineffective species of the form $(AlSO_4)^+$ are increasingly predominant. Matijević points out that at low pH in the presence of sulphate, the residual hydrated Al^{3+} ion uncomplexed with SO_4^{2-} is the predominant species effective during destabilization. Hence, since the $Al(SO_4)^+$ complex has no significant adsorptive capacity, the higher the sulphate concentration and the lower the pH, the less effective is destabilization.

One can summarize the effect of the presence of sulphate anions on destabilization with metal coagulants as follows: at pH values greater than approximately 7,0 added sulphate has very little effect since minimal displacement of OH^- occurs. As the pH is lowered SO_4^{2-} progressively displaces OH^- forming complexes with an {Al}:{OH} ratio of 1:1,25(35) compared to complexes with an {Al}:{OH} ratio of 1:2,5(34).

However, the presence of SO_4^{2-} in the coordination sheath of the metal ion complex renders the resultant complex with similar charge characteristics to the Al-OH complex at optimum pH in the absence of SO_4^{2-}. If the pH is excessively lowered $Al(SO_4)^+$ species predominate and destabilization is minimal. From this it is appreciated that the effect of adding sulphate to a hydrolyzed metal ion system does not shift the optimum pH but merely extends it to the acid side to an extent depending on the sulphate concentration present. Within the (spread) optimum pH range there is a gradual transition from Al-OH to $Al\text{-}SO_4\text{-}OH$ species as the pH is lowered, each species retaining similar charge characteristics and destabilization efficacy.

One can further add that the pH required for maximum precipitation of aluminium compounds is lower in the presence of sulphate anions. De Hek et al(19) attribute this principally to a catalytic reaction of SO_4^{2-} on precipitate formation. That is, although the sulphate ion enters into complexing reactions with aluminium, on precipitate formation the hydroxyl ion penetrates the inner coordination sphere. Hence on growth of the precipitate, sulphate anions are progressively *pushed* outwards serving to initiate further precipitate growth by complex formation with aluminium and hydroxyl ions.

4.3.3 Effect of Phosphate

In the preceeding section it was seen that the effect of sulphate anions is to extend the optimum pH range to the acid side to an extent dependent on the sulphate concentration present. With phosphate anions the effect is somewhat different. As seen in Figure 4.9(38), with increasing phosphate concentration the effect is to *shift* the optimum pH to the acid side, to a value dependent on the phosphate concentration present.

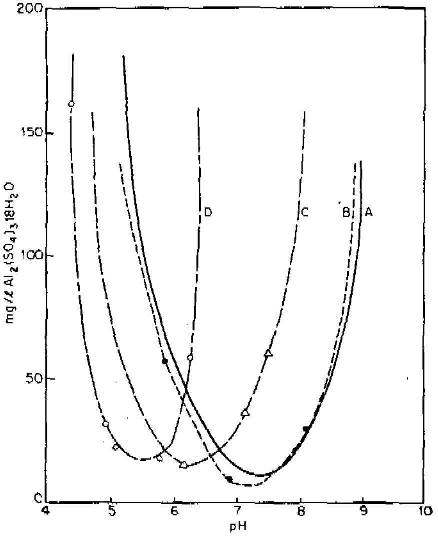


FIGURE 4.9: Effect of Orthophosphate on pH Zone of Coagulation. Points on the Curves Represent the Alum Dosage Required to Reduce 50 mg l^{-1} of Clay Turbidity to One-Half its Original Value. Curve A, Alum Alone, No PO_4; Curve B, 4,8 mg l^{-1} PO_4 Added; Curve C, 48 mg l^{-1} PO_4 added; Curve D, 475 mg l^{-1} PO_4 Added. Presence of Orthophosphate Displaces the pH Zone of Coagulation Towards the Acid Side. (After Packham(38)).

At pH values of 7,0 and above, in the presence of phosphate the principal ligands are OH^-, HPO_4^{2-} and PO_4^{3-}. Phosphate species, through their displacement of OH^- ions, render the complex more negative than if hydroxyl ions were the only ligands present; such phosphate species are strong coordinators with metal ions. At lower pH values phosphate species are changed to singly charged $H_2PO_4^-$ and, furthermore, the availability of OH^- is reduced. Hence, to retain the same overall charge characteristics as at the optimum pH value when no phosphate is present, the optimum pH in the presence of phosphate is lower.

From the above argument it is appreciated that, as the phosphate concentration is increased, because of a greater statistical opportunity for incorporation of phosphate species in the coordination sheath, the lower will be the optimum pH for destabilization.

4.3.4 Phosphorus Removal in Wastewater Treatment

4.3.4.1 General

Prior to the development of synthetic detergents, phosphorus concentrations in wastewater discharges typically varied from 2 to 4 mg l^{-1}. Most of the phosphorus was contributed by human wastes as a result of metabolic breakdown of proteins. With the advent of synthetic detergents, which use large amounts of polyphosphate *builders*, phosphorus concentrations have risen to average values of the order 8 mg l^{-1}.

Phosphorus concentrations in wastewater discharges have become of serious concern in many areas due to the major rôle played by phosphorus in promoting eutrophication. The evolution of the activated sludge process is such that several new plants have been designed on the basis of not only nitrification - denitrification but also biological phosphorus removal (see, for example, Barnard(2)). With such plants a high percentage of phosphorus is incorporated in the biological mass and is removed from the system via sludge wastage. The effluent contains typically 0,5 mg l^{-1} phosphorus which, in some cases, is suitable for discharge to watercourses without fear of eutrophication problems, whereas in other instances, this reduced level may not be sufficient to control eutrophication. This would be especially so where the treated wastewater discharge is high compared to the capacity of the receiving body of water.

In existing plants, where biological phosphorus removal has not been accomodated, effluent phosphorus concentrations will be of the order 5 to 8 mg l^{-1}. Here, such excessive phosphorus levels may pose a serious eutrophication problem.

In cases where phosphorus concentrations in wastewater discharges are excessive with respect to the capacity of the receiving body of water, a solution is to add metal coagulants. The phosphorus precipitates formed by this procedure are separated from the effluent stream either prior to discharge or within the receiving body of water. In the latter case phosphorus is fixed by precipitate formation and is incorporated in the sludge zone of, say, the lake receiving the discharge. Here, it is important that the coagulant species incorporated in the precipitate are not reduced under anaerobic conditions. For this reason, where coagulant addition to the effluent immediately prior to discharge is practiced, aluminium sulphate is to be preferred to, say, ferric sulphate. In the latter instance, reduction of Fe(III) species to Fe(II) under anaerobic conditions existing in the sludge zone will give rise to redissolution and release of phosphorus back into the water.

In some cases metal coagulants are added within the biological process. However, this may give rise to pH inhibition problems and/or interfere with subsequent biological sludge conditioning (for example, aerobic(1) or anaerobic digestion). Furthermore, additional problems of sludge disposal may result: Baillod et al(1) report that adding aluminium sulphate at the head of an activated sludge system for phosphorus removal yielded 50% more sludge on a dry weight basis and 16% more on a volumetric basis. The Al:P molar ratio applied was 1,7:1.

Problems of coagulant addition to biological systems may be avoided by dosing the final effluent prior to rapid sand filtration. The advantages here are that coagulant addition serves to enhance the polishing function of the filter and phosphorus precipitates are retained within the filter. The problem of disposal of the coagulant generated sludge is now confined to a single separate stream: the filter backwash.

Coagulant addition has been applied to biological processes other than activated sludge to effect phosphorus removal. For example, coagulants applied to stabilization pond effluents(12, 45) (in conjunction with, say, a flotation process) effect algal, COD, nitrogen as well as phosphorus reduced loads to receiving waters. On the smaller scale, Brandes(11) describes an automatic alum dosing system for households served by septic tanks - of particular interest in areas where infiltration to a body of water is likely and eutrophication of concern.

The following sections discuss certain chemical aspects of phosphorus removal with metal coagulants.

4.3.4.2 Phosphorus Precipitation With Aluminium Coagulants

There exists a stoichiometric relationship between the mass of aluminium added and the mass of phosphorus precipitated. In molar terms, the Al:P ratio has been reported as varying from 1,4 to 3,44(1, 11, 12, 20). Assuming that each reported value corresponds to the optimum pH value for phosphorus removal (see later) one can offer that the differences in reported Al:P ratios are due to different wastewater constituents (for example, the effluent from activated sludge plants after secondary sedimentation, algal laden stabilization pond effluents and so on) and/or different methods of solid liquid separation (for example, sedimentation, flotation, filtration, etc.) which may require different conditions of coagulant addition. In other words, with such applications it is perhaps not sufficient to form a stoichiometric aluminium-phosphorus precipitate. A settleable or filterable floc incorporating the precipitate is also required.

Precipitation of phosphorus under stoichiometric conditions will effect removals of the order 90% (see Figure 4.10(12)). For higher removals an excess of coagulant is required. As seen in Figure 4.10, a further advantage of adding coagulant in excess of stoichiometric requirements is that phosphorus removal is effected over a wider pH range. This is explained in terms of competition between coordinating ligands: At a given pH value, at any particular time there will be a certain amount of phosphorus complexed with metal coagulant; the optimum pH represents that pH where the largest fraction of complexes are formed with phosphorus. If the metal coagulant dosage is higher than the stoichiometric requirements then there will be a correspondingly wider pH range over which most of the phosphorus will be complexed. Note that beyond a certain maximum, no further phosphorus removal is obtained with increased coagulant dosage.

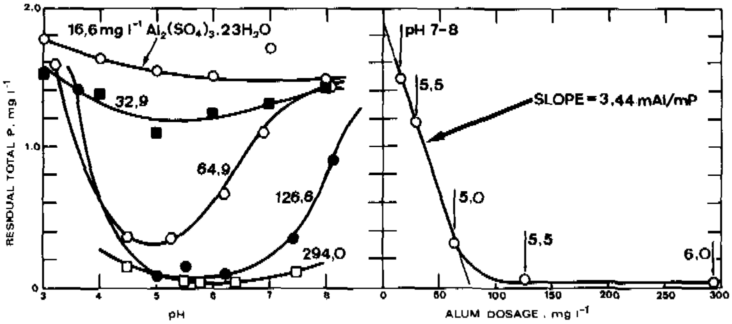


FIGURE 4.10: Demonstrating the Stoichiometry of Phosphorus Removal With Metal Coagulant Dosage. Increasing The Coagulant Dosage Widens the pH Range of Effective Removal (After Bratby(12)).

The optimum pH for phosphorus removal using aluminium coagulants is normally within the range 5,5 to 6,0(12, 20, 45). Again, slight differences in reported values are probably due to differences in wastewater constituents.

Ferguson and King(20) presented a model by which the aluminium sulphate dosage to effect a given phosphorus removal is obtained together with acid or base requirements for pH adjustment. The model requires knowledge of initial alkalinity and initial phosphorus concentration. From Figure 4.11(20), valid for an initial pH of 7,5, it is seen that two conditions are accomodated. The first represents stoichiometric removal where the dosage required for a 1 mg l^{-1} phosphorous residual is determined. The second represents the conditions for lowest phosphorous residual (0,03 mg $l^{-1}P$) corresponding to an overdose of 60 mg l^{-1} aluminium sulphate beyond that required for stoichiometric removal. It is emphasized(20) that such a model should not be considered a substitute for jar test or pilot plant evaluation of a particular wastewater application. However, it can provide a reliable guide for an experimental program and for preliminary chemical cost evaluations. For example, referring to Figure 4.11, for an initial phosphorus concentration of 10 mg l^{-1}, no acid or base is required for pH adjustment with initial alkalinities from 1,3 to 6,4 meq l^{-1} for removal in the stoichiometric zone (to 1 $mgl^{-1}P$ residual). The alum dosage required is 130 mg l^{-1}. However, a quantity of 2,3 meq l^{-1} acid (5,0 to 2,7 meq l^{-1} at 200 mg l^{-1} alum) would be required to reach the pH 6 boundary for the lowest residual zone. An initial alkalinity of 1 meq l^{-1} would require 0,9 meq l^{-1} base for maximum removal with 200 mg l^{-1} alum. In this case the use of sodium aluminate may be preferable to aluminium sulphate, although it has been reported(29) that alum is more effective than sodium aluminate in phosphorus precipitation. However, in this latter case there may have been a pH effect inherent in the results. With an initial phosphorus concentration of 10 mg l^{-1}, no acid or base is required for maximum removal with initial alkalinities from 1,9 to 2,7 meq l^{-1}.

The model of Ferguson and King briefly described above, corresponds closely to a relationship presented by Shindala and Stewart(45) where the required aluminium sulphate dosage (C, mg l^{-1}) is related to influent and desired residual phosphorus concentrations (P_i and P_e, mg l^{-1} as P) at an optimum pH of 5,5 (for municipal wastewater stabilization ponds) as follows:

$$C = P_i/(0{,}06\ P_e + 0{,}0431) - 8{,}0 \qquad (4.1)$$

For example, with an initial phosphorus concentration of 10 mg l^{-1} as P, the alum dosage required for the lowest residual concentration of 0,03 mg l^{-1} as given above is calculated from Eq. (4.1) to be 215 mg l^{-1}. From Figure 4.11 the dosage is predicted to be 200 mg l^{-1}.

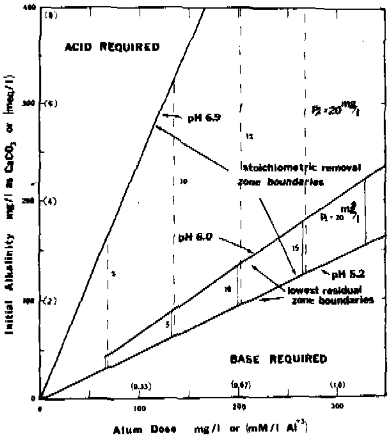


FIGURE 4.11: Relationship Between Alum Dosage and Initial Alkalinity Showing Regions Where pH Adjustment is Needed For (i) Stoichiometric Removal, Zone 1: 1 mg l^{-1} P Residual and (ii) Lowest Residual, Zone III (0,03 mg l^{-1} P Residual). From Ferguson and King(20), with Permission of the Water Pollution Control Federation.

Other sources of aluminium besides aluminium sulphate used for phosphorus removal have been powdered aluminium oxide (γ - Al_2O_3)(26) and *activated red mud.* This latter is the waste product from the Bayer process for extraction of aluminium sulphate from bauxite. Activation is by removal of sodalite compounds with hydrochloric acid. The quantity of HCl required is approximately 17% on a dry (mud) weight basis. Shiao and Akashi(44) report the long contact times required: up to 2 hours for 72% phosphorus removal. The suitability of such products depends very largely on their availability, comparative chemical costs and respective efficiencies.

4.3.4.3 Phosphorus Precipitation With Iron Coagulants and/or Lime

The dosages of iron coagulant (for example, ferric sulphate and ferric chloride) applied to precipitate phosphorus(27), expressed as a Fe:P molar ratio, are of a similar order to those for aluminium sulphate given in the preceeding section. The optimum pH is approximately 4,8(45).

Cavagnaro et al(13) and Kavanaugh et al(27) have reported the benefits of combined lime and iron coagulant usage in precipitating phosphorus. With lime, phosphorus precipitation is complete when the dosage is such as to raise the pH to 9,5 to 10,0. However, separation of the pinpoint precipitates formed is difficult unless the pH is further raised to 11,0 to 11,5. A disadvantage of such a procedure is that the lime dosage necessary to raise the pH to 11,5 may be twice that necessary for phosphorus precipitation. A solution(13) is to increase the pH with lime to a value sufficient for phosphorus precipitation (9,5 to 10,0) together with iron coagulant to aid flocculation of the precipitates formed. Using ferric chloride, Cavagnaro et al found that dosages in excess of 4,2 mg l^{-1} as Fe did not effect a significant improvement in performance; this dosage was therefore adopted as optimum for this particular application.

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5

Destabilization with Polyelectrolytes

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5.0 INTRODUCTION

Polyelectrolytes, as shown in Section 3.2, contain functional groups along their *backbone* which may or may not carry a charge. If the polyelectrolyte is charged, the groups may be such as to give an anionic character to the chain, a cationic character or an ampholytic character, where both anionic and cationic charged sites are present. The intensity of charge carried by the polyelectrolyte is dependent on the degree of ionization of the functional groups, or on the degree of copolymerization or substitutions: both of these are usually collectively described as the extent of hydrolysis.

The extent of polymerization of the polyelectrolyte is characterized by the molecular weight. High molecular weights signify long chains, whereas low molecular weights indicate short polyelectrolyte chains.

Functional groups along the polyelectrolyte chain, besides the possibility of carrying a charge, are also sites which possess the property of being adsorbed. Therefore, it is understandable that destabilization by polyelectrolytes could involve a mechanism combining both charge effects and effects due to adsorption.

Polyelectrolytes are effective in enhancing the rate of orthokinetic flocculation (see Chapter 7) when added to a system already destabilized with, say, metal coagulants, as shown below (adapted from Kitchener(31)):

$$\begin{array}{c}\text{Stable}\\ \text{Colloid}\end{array} \xrightarrow[\text{coagulant}]{+\ \text{inorganic}} \begin{array}{c}\text{unstable}\\ \text{colloid}\end{array} \xrightarrow[\text{time)}]{\text{(conditioning}} \text{flocs} \xrightarrow[\text{(conditioning)}]{+\ \text{polyelectrolyte}} \begin{array}{c}\text{large}\\ \text{flocs}\end{array}$$

Polyelectrolytes may also be effectively applied as primary coagulants, as shown below(42):

$$\begin{array}{c}\text{Stable}\\ \text{Colloid}\end{array} \xrightarrow[\text{(conditioning time)}]{+\ \text{polyelectrolyte}} \text{flocs}$$

Furthermore, there are instances where polyelectrolytes are effective in precipitating substances dissolved in solution.

From the above comments, it is appreciated that the destabilization mechanism operative with polyelectrolytes is complex and cannot be collectively ascribed to one particular phenomenon. For a given system, there may be a dominance of charge effects, or adsorption or chemical reactions at the functional groups. The predominance or relative combination of each phenomenon depends on the characteristics of the system and of the added polyelectrolyte.

This Chapter will discuss, in turn, mechanisms of destabilization by polyelectrolytes; the use of polyelectrolytes as primary coagulants; their use as flocculant aids where they are added to a system already destabilized; and as sludge conditioners where they are added to a system where dehydration reactions are required.

5.1 MECHANISMS OF DESTABILIZATION

5.1.1 General

As stated above, there is no single mechanism of destabilization by polyelectrolytes which may be considered applicable in all instances. However, it is possible to set down two principal mechanisms which in some instances may be operative conjointly, whereas in others the predominance of one over the other is fairly simple to identify. In some cases, the two phenomena may operate in opposition. The two mechanisms are based on (i) a bridging model, where polyelectrolyte segments are adsorbed on the surfaces of adjacent colloids thereby binding them together and (ii) a model whereby ionic polyelectrolytes, bearing a charge of opposite sign to the suspended material, are adsorbed and thereby reduce the potential energy of repulsion between adjacent colloids. Associated with this second model is the phenomenon described in Chapter 2 where oppositely charged polyelectrolytes, by their presence in the double layers of particulate material, reduce the interaction energy. With (i) it is seen that (ii) may support the action of the other, or oppose it, depending on whether there is strong electrostatic attraction between the polyelectrolyte and colloid surface. With (ii) it is appreciated that if (i) contributes to destabilization, it will always support the action of the other.

The two mechanisms introduced above are referred to as the *bridging* mechanism and the *electrostatic patch mechanism* respectively. Although, for convenience, they will be described separately below, it should be reiterated that the overall mechanism of destabilization in some instances may be contributed to by both phenomena.

5.1.2 The Bridging Mechanism

The bridging mechanism of destabilization by polyelectrolytes has been an accepted phenomenon for some time (27, 41, 58). The principal basis for acceptance lies in the ability of charged polyelectrolytes to destabilize particles bearing the same charge(22, 56, 58). Furthermore, direct evidence is available(4) whereby electron micrographs have identified polyelectrolyte bridges between particles.

Akers(2) presents several stages in the bridging mechanism as follows:

(i) Dispersion of polyelectrolyte in the suspension;
(ii) Adsorption at the solid-liquid interface;
(iii) Compression or *settling down* of the adsorbed polyelectrolyte and
(iv) Collision of adjacent polyelectrolyte coated particles to form bridges and thereby increasingly larger flocs.

Each of these stages, schematically represented in Figure 5.1 (adapted from Akers(2)), are discussed in detail below:

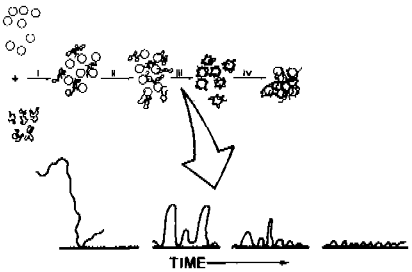

FIGURE 5.1: Stages in the Bridging Mechanism of Destabilization with Polyelectrolytes: (i) Dispersion; (ii) Adsorption; (iii) Compression or Settling Down (See Inset) and (iv) Collision. (Adapted From Akers(2)).

5.1.2.1 Dispersion in the Suspension

Because of their high molecular weights, polyelectrolytes in solution exhibit high viscosities (see Section 3.2.4.2) and low diffusion rates. Since adsorption of polyelectrolytes to particle surfaces is essentially irreversible, for adsorption to occur evenly on all particles it is essential that the polyelectrolyte be dispersed evenly throughout the suspension(1). Furthermore, as the subsequent adsorption reaction is usually much faster than the rate of diffusion, it is necessary to disperse the polyelectrolyte throughout the suspension as quickly and efficiently as possible. This is accomplished during the rapid mixing stage (Chapter 6) where a *short* vigorous mixing environment is required to effect dispersion in the shortest practicable time.

5.1.2.2 Adsorption at the Solid-Liquid Interface

After step (i), where polyelectrolytes have diffused to the solid-liquid interface, adsorption of initially one functional group will occur while the rest of the chain is for a while momentarily free and extends into the solution(54) (see inset to Figure 5.1). As time proceeds, due to continuous Brownian movement, the chain becomes successively attached at more points along its length until eventually there are no *dangling* ends extending into the solution phase. The configuration is now one of a number of pendant *loops* extending some distance out from the particle surface.

The mechanism of adsorption of polyelectrolyte segments to a solid surface depends on both the chemical characteristics of the polyelectrolyte and the adsorbent surface. For example, adsorption could be due to cation exchange, as reported for adsorption of cationic polyelectrolytes on clay particles(39, 40, 58); electrostatic linkages, hydrogen bonding or ionic bonding as variously suggested by several workers(28, 38, 42, 44, 45, 46, 55) for cases of anionic polyelectrolyte adsorption to clays.

As mentioned in Section 2.3, polyelectrolyte adsorption is described by the Simha-Frisch-Eirich (S.F.E.) adsorption isotherm(18). The Langmuir isotherm theoretically represents the S.F.E. isotherm for the special case of $\beta = 1$ (where β = the number of segments per polymer molecule attached to the adsorbent surface). However, polyelectrolyte adsorption often follows the Langmuir isotherm, even when estimated values of β are, for example, of the order 470 to 1660(18). Instances where the Langmuir isotherm may be inadequate are at low polyelectrolyte concentrations.

In the case of polyelectrolytes and particles carrying charges of like sign, adsorption may be strongly dependent on ionic strength. For example, for the case of hydrolyzed polyacrylamide and negatively charged kaolinite clay surfaces, adsorption has been found to be strongly dependent on the calcium-ion concentration(11). In general, with calcium ions a critical concentration of approximately 10^{-3} M is often found, which corresponds to a hardness in excess of 100 mg l^{-1} as $CaCO_3$. In some cases, the presence of cations such as Ca^{++} may have the effect of complexing with polyelectrolyte functional groups(64) thereby aiding adsorption of, say, negative particles by anionic polymers, by a cation bridging effect(37).

Ionic strength may influence adsorption by two effects: (i) reduce repulsion between similarly charged particle surfaces and polyelectrolyte segments, thus permitting adsorption to occur and (ii) reduce the size of the polyelectrolyte coil (see Section 3.2.4.2) thus permitting more polyelectrolyte chains to be accomodated on the particle surface.

Adsorption is effectively irreversible(61): Although the energy of adsorption at any particular site may be low and under normal circumstances may indicate a probability of desorption, the chance of desorption occurring simultaneously at a number of sites is low. Although under normal conditions of destabilization with polyelectrolytes, desorption of the whole chain from the particle surface does not occur, displacement may be induced by, for example, suitably adjusting pH conditions or adding a sufficiently high concentration of surface competitor (e.g. sodium tripolyphosphate)(31).

5.1.2.3 *Compression of Adsorbed Chains*

The probability of a successful *bridge* forming between two adjacent particles depends on the configuration of the adsorbed polyelectrolyte at the surface. As stated previously (and schematically shown in Figure 5.1) from the onset of adsorption, progressively greater numbers of polyelectrolyte segments will become adsorbed on the particle surface and, consequently, the polyelectrolyte chain will become compressed to the surface. The polyelectrolyte layer requires a finite time to become compressed and initially, will consist of long loops. It is during this initial period, where loops are longest and extend the furthest into solution, that bridging is most effective. With extensive adsorption of segments to the surface, the polyelectrolyte chain progressively assumes a flatter configuration until the extent of double layer repulsion exceeds the size of the loops. This effect is particularly pronounced for dilute colloidal suspensions where a statistically longer time is available for compression of polyelectrolyte loops. A possible solution is to add polyelectrolyte in stages(1) thus ensuring that large loops are retained for periods sufficient for bridging to occur.

The configuration of the adsorbed polyelectrolyte chain depends upon the size of the polyelectrolyte (molecular weight); its structure; flexibility; charge density (% hydrolysis); interaction energy between polyelectrolyte and particle surface; chemical nature and physical spacing of adsorption sites on the particle surface and the competition between polyelectrolyte and other adsorbing molecules in solution(18).

As regards molecular weight, in general where the bridging mechanism is predominant, an increase in chain length gives rise to an increase in the *optimum* polyelectrolyte/solid ratio. This is because longer chains do not lie as flat on the surface as shorter chains and, therefore, individual chains do not occupy as many adsorption sites. Therefore, bridging is more efficient with polyelectrolytes of higher molecular weight since loops will tend to extend further into solution. This is evident from the fact that, with appropriate systems, for a given applied polyelectrolyte concentration, the higher the molecular weight the higher is the efficiency of destabilization (assessed in terms of say, size of flocs, settling rates, filterability and so on). As stated in Section 3.2.4.2 the upper limit of molecular weight is governed by practical considerations of dissolution.

Flexibility of polyelectrolyte segments influences the size of the pendant loops: a relatively inflexible polyelectrolyte chain will tend to be attached by only a few segments and the loops will tend to be longer than for a relatively flexible chain.

Considering percentage hydrolysis (or charge density); as was pointed out in Section 3.2.4.2, the higher the charge density the greater is the repulsion between adjacent segments and the more extended is the polyelectrolyte chain for a given molecular weight. The more extended the polyelectrolyte the further should the pendant loops extend into solution and the more effective should be the bridging mechanism. However, unlike molecular weight there is an upper limit to the charge density, beyond which electrostatic repulsion (in the case of polyelectrolyte and solid surface of similar charge characteristics) will effectively retard adsorption. Michaels(41) found that with polyacrylamides a 30% degree of hydrolysis was optimal; this value providing a compromise between extended loops and polyelectrolyte surface repulsion.

Ionic strength considerations to a certain extent follow a similar reasoning: as stated in Section 5.1.2.2, increasing ionic strength tends to increase the efficiency of polyelectrolyte adsorption. Furthermore, increasing ionic strength reduces the range of inter-particle repulsion (after polyelectrolyte adsorption) so that particles have a statistically high opportunity of approaching close enough together for bridging to take place before extensive compression of polyelectrolyte segments occurs. However, on the other hand, the greater the ionic strength, the less extended is the polyelectrolyte chain and the shorter is the range of extension of polyelectrolyte loops. Again, optimum conditions will be governed by a balancing of the above factors.

5.1.2.4 Bridge Formation

After adsorption has taken place as described in the preceeding sections, polyelectrolyte loops extending into solution from the particle surfaces will further become adsorbed onto adjacent particles thus forming a number of bridges. The strength of the flocs thus formed depends on the number of bridges formed, which in turn is dependent on the number of loops available. From preceeding discussions, the number of loops available for mutual adsorption between adjacent particles, before extensive compression takes place and the loops are within the bounds of the respective double layers, is dependent on a number of factors related to both the suspension and the added polyelectrolyte.

A factor of crucial importance during bridging is the availability of adsorption sites on particles to accomodate polyelectrolyte loops from neighbouring particles. Such availability depends on the concentration of polyelectrolyte added: If an excess of polyelectrolyte is added, too many adsorption sites per particle will be occupied and bridge formation is prevented: the particles effectively become restabilized.

La Mer and Smellie(33, 34, 35, 36, 62, 63) postulated that optimum flocculation occurs when the fraction of surface covered by polyelectrolyte, θ, is one half, i.e. $\theta = 0{,}5$. However, many workers have found that maximum flocculation occurs at θ values much less than 0,5, typically ranging from 0,09 to 0,33(11, 32). In any case, it has been suggested(18) that the parameter θ is relatively unimportant in determining the degree to which a suspension will be destabilized when related to other factors such as particle concentration, inter-particle interactive forces, ionic strength, polymer configuration in the adsorbed state and intensity and duration of mixing. However, for many systems a stoichiometric polyelectrolyte dosage-particle concentration relationship often exists(12, 52, 60) indicating the predominance of adsorption during destabilization reactions.

Intense mixing may disrupt polyelectrolyte bridges and give rise to desorption and/or rearrangement of looped chains on the particle surface. It is evident therefore that although efficient mixing is required on polyelectrolyte addition to a suspension, as stated in Section 5.1.2.1, the mixing should not be too violent nor for too long a period. The addition of dilute polyelectrolyte solutions is clearly of advantage. The requirements for rapid mixing are dealt with in Chapter 6.

5.1.3 The Electrostatic Patch Mechanism

For the case of non-ionic and anionic polyelectrolytes applied to a negatively charged colloidal dispersion, a destabilization mechanism described by the bridging model adequately accounts for the phenomena taking place. Indeed, in many cases it would be difficult to account for the phenomena by a mechanism other than some form of bridging(25). However, for the case of charged polyelectrolytes applied to dispersions with particles carrying surface charges of opposite sign, the bridging model is often inadequate. Such systems include cationic polyelectrolytes applied to a negative colloidal dispersion and could include anionic polyelectrolytes applied to dispersions destabilized with metal coagulants$^{(59)}$ i.e. as flocculant aids to particle-metal hydrolysis product aggregates, which may be positively charged.

Kasper$^{(30)}$ and Gregory$^{(24)}$ independently questioned the exclusivity of the bridging model. For systems where strong electrostatic attraction between polyelectrolyte and particle surface exists, they propose an electrostatic patch mechanism. Rather than adsorption of polyelectrolyte at only a few sites, with the remainder of the chain extending into solution in the form of closed loops, virtually complete adsorption of added polyelectrolyte onto the particle surface takes place with such systems. The adsorbed polyelectrolyte chains thus form a charge mosaic with alternating regions of positive and negative charge as shown schematically in Figure 5.2$^{(24)}$. Destabilization occurs when the charge mosaics of adjacent particles align to provide strong electrostatic attraction. It is seen that the electrostatic patch model as described above bears a resemblance to the electrical double layer model of colloid destabilization, where the adsorption of counter-ions in the Stern layer brings about a reduction in the potential energy of repulsion between particles.

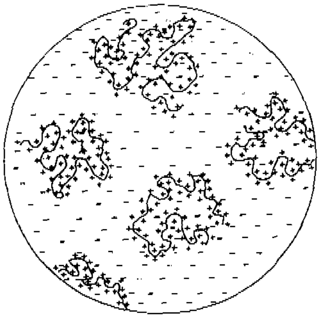

FIGURE 5.2: Possible Arrangement of Adsorbed Polycations on a Particle With Low Negative Surface Charge Density. (From Gregory$^{(24)}$, with Permission of the Academic Press).

For high energies of adsorption, $1,0kT < E_{ss} < 10,0kT$ (where E_{ss} = energy of interaction between polyelectrolyte segments and particle surface, k = Boltzmann's constant and T = absolute temperature) as exists with polyelectrolyte segments attracted to oppositely charged surfaces, the possibility of bridging via long loops or tails has been suggested as unlikely (30), even for polyelectrolytes of high molecular weight. However, there are instances where high molecular weights do give rise to increased destabilization efficiency in such systems. Gregory(25) explains this by a consideration of kinetic effects:

As explained in Section 5.1.2.3, adsorption of a polyelectrolyte chain takes place by a series of individual attachments over a finite period of time. As more segments are adsorbed, the configuration of the adsorbed chain becomes progressively flatter and loops become less extensive until some equilibrium state is reached. In the interim between the initial stages of adsorption to the attainment of the equilibrium configuration, there is an interval of time within which polyelectrolyte loops may extend sufficiently far into solution for bridging to take place between adjacent particles.

For a bridging mechanism to be effective, destabilization would need to be virtually complete within the time required for loops to be compressed and be ineffective for bridging. This would be greatly influenced by the collision frequency of particles and, therefore, is directly related to particle concentration: At high particle concentrations a given particle will collide with many others while polyelectrolyte loops are still in a relatively extended state.

Gregory(24, 25) provided evidence of the above mechanism for the destabilization of latex particles using cationic polyelectrolytes. At low particle concentrations, the destabilization mechanism is as described by the electrostatic patch model. Here, since bridging is of negligible consequence, the molecular weight of the polyelectrolyte would have little importance: in view of the difficulty of dissolving high molecular weight products, a polyelectrolyte of low molecular weight is probably preferable. Furthermore, since charge effects are predominant, the use of polyelectrolytes of high charge density should prove most effective.

At high particle concentrations, considerable bridging effects are evident and high molecular weights should prove beneficial, as discussed in previous sections. The results of Gregory's work(25) showed that bridging is negligible for particle concentrations less than of the order 10^{14} particles l^{-1}. He points out that typical river waters contain less than of the order 10^{12} particles l^{-1}. In such applications therefore, if polyelectrolytes as primary coagulants are considered, the use of high molecular weight cationic polyelectrolytes is not justified. For more concentrated suspensions such as is the case with sludge conditioning, if cationic polyelectrolytes are used those of higher molecular weight would probably give best results.

5.1.4 Summary of Characteristics of Mechanisms

To conveniently summarize the characteristics of the two mechanisms described respectively by the bridging model and electrostatic patch model, Table 5.1 comprises a compilation of the principal points presented in preceeding sections.

TABLE 5.1 : SUMMARY OF CHARACTERISTICS OF MECHANISMS

PARAMETER	INFLUENCE OF INDICATED PARAMETER ACCORDING TO MODEL	
	BRIDGING	ELECTROSTATIC PATCH MODEL
MOLECULAR WEIGHT OF POLYELECTROLYTE	The higher the M.W., the more effective the bridging. Upper limit dictated by dissolution	In strict accordance with model M.W. should have no effect. Improved performance evident in some cases with higher M.W. due to onset of bridging
CHARGE DENSITY, OR PERCENTAGE HYDROLYSIS	The higher the charge density, the more effective is bridging due to larger loops. Upper limit dictated by electrostatic repulsion between polyelectrolyte and surface of particle, where respective charges similar, during adsorption	The higher the charge density, the more pronounced will be the charge mosaic and the more effective will be destabilization
POLYELECTROLYTE OF SIMILAR CHARGE TO PARTICLE SURFACE	Destabilization by bridging mechanism	Electrostatic patch mechanism inoperative
POLYELECTROLYTE OF OPPOSITE CHARGE TO PARTICLE SURFACE	Destabilization by bridging mechanism possible	Destabilization by electrostatic patch mechanism possible
NON-IONIC POLYELECTROLYTE	Destabilization by bridging mechanism	Electrostatic patch mechanism inoperative
AMPHOLYTIC POLYELECTROLYTE	Destabilization by bridging mechanism possible	Destabilization by electrostatic patch mechanism possible
EFFECTIVE SURFACE CHARGE AT OPTIMUM CONDITIONS FOR DESTABILIZATION	Usually not zero	Not necessarily zero
EFFECTIVE SURFACE CHARGE WITH EXCESS POLYELEC TROLYTE ADSORPTION	Possible reversal of charge by excessive adsorption. Destabilization still possible	As for bridging
POLYELECTROLYTE CONCENTRATION	Optimum destabilization when surface site coverage $\theta \simeq 0,5$	Optimum destabilization not limited by residual adsorption sites: However θ probably $\sim 0,5$
EXCESSIVE POLYELECTROLYTE ADDITION	At excessive dosages particles restabilized by complete site coverage or charge reversal	At excessive dosages possible restabilization from charge reversal
MIXING	Important for polyelectrolyte to be adsorbed evenly on particles. Mixing should be short and vigorous at the time of polyelectrolyte addition. If mixing too violent or for too long a period desorption and/or rearrangement of adsorbed chains could give rise to restabilization	Essentially as for bridging
PARTICLE CONCENTRATION	Bridging most effective the higher the particle concentration. At low concentrations a longer time is available for compression	At high concentrations, because of kinetic effects, bridging mechanism likely. At low concentrations $(\sim 10^4/\ell)$ electrostatic patch mechanism possible
IONIC STRENGTH	High ionic strength aids adsorption by reducing electrostatic repulsion in the case of polyelectrolytes and particles of opposite charge, and reducing size of polyelectrolyte coil thus permitting adsorption of more segments ; aids destabilization by reducing electrostatic repulsion between particles of like charge: can impede bridging by constricting polyelectrolyte loops	High ionic strength probably aids destabilization by reducing repulsive interaction energy between polyelectrolyte adsorbed particles

5.2 POLYELECTROLYTES AS PRIMARY COAGULANTS

5.2.1 General

There are many instances where polyelectrolytes have been employed as primary coagulants, effectively replacing the use of metal coagulants for this purpose. Such applications include treatment of waters predominantly turbid or coloured with humic substances, removal of microorganisms and various industrial applications. In cases where replacement of metal coagulants by polyelectrolytes is possible, the potential advantages are as follows(5): (i) soluble metal-ion species carry-over from sedimentation basins etc. is prevented; (ii) the need for extensive pH adjustment (and subsequent readjustment) is obviated; (iii) carry over of light flocs such as those formed with metal coagulants is minimised; (iv) sludge volume to be ultimately disposed of is reduced and (v) the amount of soluble anions are reduced.

The following sections present various examples where polyelectrolytes have been successfully applied as primary coagulants.

5.2.2 Turbidity Removal With Polyelectrolytes

Polyelectrolytes have been applied successfully as primary coagulants in a number of cases to reduce turbidity of surface waters: Robinson(57) investigated the use of polyelectrolytes in clarifying highly turbid waters (maximum turbidity approximately 5 000 JTU). Using solid and liquid cationic, nonionic and anionic types, he found that the cationic and nonionic types gave very good results; comparable to aluminium sulphate whereas the anionic types did not produce the required degree of clarification. With the cationic types, dosages ranged from 1 to 4 mg l^{-1} depending on the raw water turbidity (range 190 to 2 000 JTU).

Shea *et al*(60), applying direct filtration to turbid waters found that a cationic polyelectrolyte (quaternary ammonium compound) was superior in performance to aluminium sulphate in terms of both technical (filter runs, effluent quality, etc.) and economic (cost per unit volume treated) aspects.

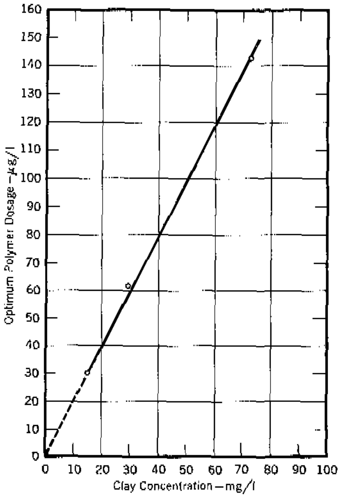

FIGURE 5.3: Stoichiometry of Destabilization of Kaolinite Clay Suspensions With Cationic Polymer PDADMA. (From Black _et al_(11), with permission of the American Water Works Association).

Black _et al_(11, 12) reported a stoichiometric reaction between polyelectrolyte dosage (diallydimethyl-ammonium chloride) and particle concentration: From Figure 5,3(11), the optimum dosage: kaolinite clay concentration was of the order 0,002 g g^{-1}. Such stoichiometry is to be expected and follows from the overriding influence of adsorption during destabilization with polyelectrolytes; whether the mechanism is governed by the bridging or electrostatic patch model. A possible exception, where stoichiometry may not be evident, would be if the mechanism was principally that of double layer repression as could exist with polyelectrolytes and particles of opposite sign. However, even though this effect is almost certainly present in such cases, there is no evidence to suggest that adsorption would not still be the predominant phenomenon promoting destabilization.

Although stoichiometric relationships as above may be gleaned from the results of several workers, it should be noted that initial turbidity is not sufficient information for an _a priori_ estimation of the polyelectrolyte dosage required. The presence of other substances in a particular water may exert an appreciable polyelectrolyte demand over and above that required for turbidity removal. Such substances, which include(7) organic colour, anionic detergents, lignins, orthophosphates and so on, react with polyelectrolytes to form soluble complexes or colloidal precipitates (See Section 5.2.1.2). For turbidity removal, therefore, the polyelectrolyte dosage is over and above that required for these substances. Furthermore, the adsorption of chemical species to particles producing turbidity, such as clays, will reduce the number of adsorption sites for polyelectrolyte and/or alter the adsorption characteristics of polyelectrolyte to the particles.

For a given particle mass concentration the optimum dosage depends on the type of material present i.e. smaller particle suspensions require higher dosages of polyelectrolyte at optimum destabilization (because of the higher total surface area). Furthermore, the larger the range of particle sizes of a given suspension , the wider is the range of polyelectrolyte dosage giving good performance. For example, with latex particles the surface area characteristics are generally more uniform and, therefore, optimum destabilization occurs at a relatively precise polyelectrolyte dosage, when compared with, say, a kaolinite clay suspension. From the results of Birkner and Morgan(8) stoichiometry is also evident with latex suspensions: using a cationic polyelectrolyte (polyethylenimine), at optimum conditions for destabilization the dosage: particle number ratio is of the order 2.10^{-12} mg.

Morrow and Rausch(43) found that cationic polyelectrolytes (polydiallyldimethylammonium chloride) were able to replace metal coagulants successfully for both low and high turbid waters. They pointed out that the often reported unsatisfactory performance of polyelectrolytes when used alone, may be due to too low velocity gradients during the rapid mixing stage (see Chapter 6). Optimum results were obtained using velocity gradients in excess of 400 s^{-1}. The lower the polyelectrolyte dosage, the higher should be the velocity gradient. For example, at a dosage of 2 mg l^{-1}, the optimum rapid mix velocity gradient was $500s^{-1}$. Using 1 mg l^{-1} the optimum velocity gradient was 750 s^{-1}. However, as stated in Section 5.1.2.4, there is an upper limit to velocity gradient. For example, in the above study, velocity gradients of 1000 s^{-1}

resulted in poor overall solids capture probably due to shearing of polyelectrolyte segments from particles.

Deeble(20) describes the use of cationic polyelectrolytes (polyamines) in clarifying a number of turbid (and coloured) waters. With turbidities ranging from 5 to 30 mg l^{-1} SiO_2 (and colour 30 to 140 mg l^{-1} Pt. Co.) dosages of polyelectrolyte from 1,5 to 9,0 mg l^{-1} reduced the turbidity and colour to approximately 1 mg l^{-1} SiO_2 and 5 mg l^{-1} Pt.Co. respectively.

5.2.3 Organic Colour Removal with Polyelectrolytes

For polyelectrolytes to be generally acceptable for water treatment applications, Packham(53) suggests that they should be capable of removing organic colour (humic substances). By conducting tests with a wide variety of commercial cationic polyelectrolytes and assessing their effectiveness in precipitating fulvic acid (the predominant humic fraction in coloured waters) he found that the polyelectrolytes varied widely in their ability to remove organic colour; as seen in Figure 5.4(53), removals ranged from 3% to 87% with optimum dosages (at maximum colour removal for each product) from 2 to 16 mg l^{-1}. Although some polyelectrolytes were effective in precipitating fulvic acids (notably polyethylenimine and an unspecified product *Primafloc C7*), in almost all cases the floc formed was very poor, settled slowly and gave rise to a high final supernatant turbidity. It was suggested that the poor flocculation characteristics were due to the fact that most polyelectrolytes do not form insoluble hydrolysis products. Therefore, they lack the advantage of metal coagulants applied to coloured or low turbid waters where hydrolysis products increase particle number concentrations thereby improving flocculation kinetics. An exception was the product *Floccotan,* a tannin based natural polyelectrolyte, which did exhibit acceptable floc formation characteristics. This product reacts with water to form an insoluble hydrolysis product. However, floccotan effected only an average colour removal.

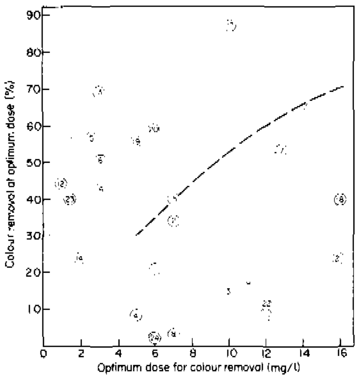

FIGURE 5.4: Precipitation of Fulvic Acid With Cationic Polyelectrolytes. Results of Screening Tests with 24 Commercial Polyelectrolytes (Fulvic Acid 10 mg/l, pH 5.5): 1, BTICL80; 2,BTICL40; 3,BTIC100 ; 4, BTIC110; 5, Catafloc; 6, Cirrasol Z; 7, Floccotan; 8, Katafloc; 9, Magnafloc R225; 10, Magnafloc LT22; 11, Magnafloc LT24; 12, Nalfloc N607; 13, Polyethyleneimine; 14, Primafloc C3; 15, Primafloc C5; 16, Primafloc C6; 17, Primafloc C7; 18, R 177; 19, RD 2180; 20, RD 2181; 21, Reten 205; 22, Reten 210; 23, Superfloc 521; 24, Wisprofloc P. (From Packham(53), With Permission of the Academic Press Inc.).

By adding montmorillonite to the systems tested, Packham found that with added clay concentrations of at least 5 mg l^{-1}, the floc characteristics were markedly improved. Hence, by adding clay to coloured and/or low turbid waters, satisfactory colour and/or turbidity removals may be achieved by adding the appropriate polyelectrolyte. From Packham's results it appears that the polyelectrolyte dosage is from 6 to 10% of the corresponding metal coagulant dosage.

Narkis and Rebhun(48, 49) describe the destabilization of humic substances with cationic polyelectrolytes (polyethylenimine(49)) to be essentially the result of chemical reactions between polyelectrolyte segments and carboxylic and phenolic groups on the humic acid molecules. Both humic and fulvic acid solutions react with the polyelectrolyte to form colloidal precipitates which may be observed as turbidity. With incrementally increasing dosage, optimum conditions of polyelectrolyte dosage required for precipitation are identified by maximum turbidity. Such optima occur at electrophoretic mobilities slightly more or less than the isoelectric point. However, the optimum dosage corresponding to the above usually does not correspond to that required for floc formation. Adding further polyelectrolyte, bridging between adjacent precipitated particles occurs and settleable, filterable etc. flocs are formed. Apparently, the polyelectrolyte required for floc formation need not necessarily be the same as that required for preliminary precipitation. Therefore, the use of sequential polyelectrolyte addition may be advantageous.

The hypothesis of chemical interactions as described above for destabilization of humic substances by polyelectrolytes, is supported by the often reported stoichiometry of the reaction. For example, Figure 5.5(21) demonstrates the stoichiometry between initial humic acid concentration and polyelectrolyte dosage required under optimum conditions of destabilization.

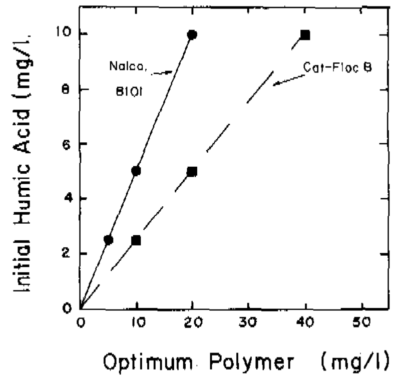

FIGURE 5.5: Stoichiometry Between Initial Humic Acid Concentration and Optimum Cationic Polyelectrolyte Dosage. (From Edzwald *et al*(21), with permission of the American Society of Civil Engineers).

As stated previously, subsequent floc formation after precipitation of humic substances with cationic polyelectrolytes, may be improved by increasing the particle concentration with clay addition. With such mixed systems the polyelectrolyte reacts first with the humic substances and only after precipitation is complete will destabilization of clay particles occur(48, 49).

Precipitation of humic acids by cationic polyelectrolytes is markedly dependent on pH. Narkis and Rebhun (49) found a non-linear relationship such that with a decrease in pH from 6,0 to 2,8, the optimum polyelectrolyte dosage required for precipitation decreased from 3 to 0,8 mg l^{-1}. This effect was attributed to a decrease in the degree of ionization of the humic molecules thus resulting in lower negative charges. Therefore, the lower the pH, the lower is the required polyelectrolyte dosage.

5.2.4 Removal of Microorganisms with Polyelectrolytes

Polyelectrolytes have been shown by several workers to be effective in the destabilization and removal of microorganisms. In general, cationic polyelectrolytes are required for effective destabilization; anionic or nonionic types usually produce markedly inferior results: Tenney <u>et al</u>(65, 66) showed that cationic polyelectrolytes were effective in destabilizing bacterial and bacterial-algal mixed suspensions. Treweek and Morgan(69) similarly found that cationic polyelectrolytes (polyethylenimine) were effective in destabilization of suspensions of E. Coli. Polyelectrolytes of the latter type, with a wide range of molecular weights (600 to 60 000, number average values), were strongly adsorbed to the bacterial cells. However, efficient destabilization was only evident with the high molecular weight samples (35 000 and 60 000). The mechanism of destabilization evident in the latter experiments was identified as that described by the electrostatic patch model. The poorer results obtained with lower molecular weight polyethylenimine species was hypothesized to be due to the small size of individual molecules and consequently their inability to neutralize the negative *E. Coli* surface and thus create positive patches. Therefore, with the low molecular weight species, the mechanism of destabilization was attributed to adsorption and thus reduction of double-layer repulsion (see Chapter 2).

Polyelectrolytes have also proved effective in destabilizing algae: Cohen et al(16), Golueke and Oswald(23) and Tilton et al(68) effectively destabilized suspensions of *Chlorella* and *Scenedesmus* using cationic polyelectrolytes. Using polyethylenimine, there appeared to be a significant increase in effectiveness with increasing molecular weights up to 2 000 (determined by viscosity measurements). However, beyond 2 000 no further improvement was evident (68). Tilton et al further point out that the polyelectrolyte dosage required for algal suspensions (*Chlorella ellipsoidia*) can be much higher than for bacterial suspensions (in their experiments 30 times the dosage requirements of *E. Coli*).

These workers tentatively attribute this difference to factors such as differences in structure of the cell envelopes of the organisms.

As seen in Section 4.2.3, significant virus removal may be effected using metal coagulants. Some workers have found adequate virus removal using cationic polyelectrolytes. For example, Thorup et al(67) studied the removal of *bacteriophage T2* and *type 1 poliovirus*. Anionic and nonionic polyelectrolytes were found to be relatively ineffective whereas cationic polyelectrolytes effected removals of up to 96%. The removal was strongly dependent on ionic strength: for at least 95% removal of T2 virus and a polyelectrolyte concentration of 1 mg l^{-1}, 0,005 M Na^+, or 0,003 M K^+, or 0,003 M Ca^{++} or 0,005 M Mg^{++} were required. With solutions containing the above ionic concentrations and with turbidities represented by 5 mg l^{-1} each of bentonite and infusorial earth, floc formation was good.

With poliovirus, removals recorded by Thorup et al were inferior to those with T2 virus: up to 36% only. Again removal was significantly ionic strength dependent.

Amirhor and Engelbrecht(3) studied the removal of bacterial virus MS2 against *E. Coli* with diatomaceous earth filtration. They found that uncoated diatomaceous earth filter media are ineffective in virus removal. However, by adding a cationic polyelectrolyte (polyamine type, molecular weight (60 000) either as a precoat to the diatomaceous earth media or applied to the suspension prior to filtration, significant virus removal was obtained.

There was a sharp optimum polyelectrolyte dosage evident in their experiments of 0,25 mg l^{-1} for $1,4.10^{8}$ pfu ml^{-1}. Beyond this dosage restabilization of the viruses occurred and removals correspondingly decreased. Similar results to the above were obtained by Chaudhuri et al(15) with removal of bacterial viruses T4 and MS2 through uncoated and cationic polyelectrolyte coated diatomaceous earth media.

5.3 POLYELECTROLYTES AS FLOCCULANT AIDS

Polyelectrolytes are widely accepted as flocculant aids, both in water and wastewater treatment applications. In water treatment they are usually added with metal coagulants to achieve some desired effect: Here the objective is not primarily that of destabilization per se (which is effected by the metal coagulants) but rather of supplementing the orthokinetic flocculation process and altering floc characteristics in terms of increasing ultimate floc size, density, permeability, compressibility, shear strength and, concomitantly, settleability and filterability; In general, the optimum polyelectrolyte dosage required for each of these criteria is essentially the same. In biological wastewater treatment applications they may be added to supplement the natural biological flocculation characteristics thereby assisting overloaded secondary sedimentation basins.

When polyelectrolytes are added to suspensions destabilized with primary coagulants, in general best results are obtained when addition is some time after primary coagulant addition. This procedure is probably preferable because primary floc particles formed on destabilization are given the opportunity to grow to an appreciable size before polyelectrolyte is added and adsorption occurs, thereby resulting in lower polyelectrolyte requirements. However, there are some instances where flocculant aid has been added with benefit ahead of metal coagulants; examples include the use of activated silica and sodium alginate(52), where such a procedure may serve to accentuate chemical interaction between polyelectrolyte and primary coagulant. Packham(52) reports that in several cases, pre-flocculant aid addition gives rise to relatively higher residual aluminium or iron concentrations in the treated water, probably due to incomplete utilization and precipitation of the metal coagulant.

Treanor(52) states that the apparent success occasionally reported when polyelectrolytes are added before metal coagulants could be explained partly by inefficient initial dispersion of the flocculant aid and thereby a delayed action effect. On the other hand, for cases where polyelectrolyte and particles are of opposite sign, addition of polyelectrolyte before metal coagulant could serve to reduce the surface charge of particles on adsorption thereby subsequently reducing the quantity of metal coagulant required to effect charge reduction.

An interesting example of polyelectrolyte addition before metal coagulant is that reported by Cooper _et al_(19): For the reduction of organic solids and COD from tannery lime-sulphide unhairing wastes, and operating at pH values of 8,0 or greater (to prevent H_2S liberation) it was found that addition of an anionic polyelectrolyte as primary coagulant, followed by a cationic polyelectrolyte and subsequently by a metal coagulant gave superior results to all other combinations tested. With the latter procedure, COD was reduced by 56% and organic solids by 98%.

The above results notwithstanding, as stated previously in most cases flocculant aid is normally added to greatest benefit after metal coagulant addition. In such instances anionic polyelectrolytes are often found to be effective, probably because primary floc particles formed by metal-hydroxide species are positively charged under most conditions(26). It should be noted that polyelectrolytes do not necessarily lead to a reduction in metal coagulant concentration since their function as flocculant aids is not primarily that of destabilization. However, the benefits derived in terms of improved settleability, filterability and reduced sludge volume generally offsets the increased chemical cost. In cases where reduced metal coagulant dosages on flocculant aid addition have been reported, the reason may be that original metal coagulant dosages were dictated by factors such as settleability requirements, rather than by destabilization.

The following presents various selected examples of polyelectrolytes applied as flocculant aids. The examples cited are by no means exhaustive but are intended to serve merely as an indication of some of the areas where such applications have been successful.

Cohen et al(16) investigated the use of several polyelectrolytes as flocculant aids using aluminium sulphate as primary coagulant applied to turbid waters. With an anionic polyelectrolyte (hydrolysed polyacrylamide), although it functioned well as a flocculant aid, no significant turbidity removal was evident without prior aluminium sulphate addition. Dosage of the polyelectrolyte was very critical: excess dosages gave rise to restabilization. Using a cationic polyelectrolyte (described as an organic polymer), apart from its effectiveness as a flocculant aid, it could be effectively used as a primary coagulant, removing not only live organisms such as algae but also substancesdissolved in solution. A nonionic polyelectrolyte (of a form similar to carboxymethylcellulose) was found to be considerably less effective than either the anionic or cationic forms used.

Black and Hannah(10), investigating (kaolinite) turbidity removal with aluminium sulphate, assessed the efficacy of the following polyelectrolytes as flocculant aids: activated silica, potato starch, anionic polyacrylamide, a cationic type, guar gum, a cationic natural polyelectrolyte, anionic carboxymethylcellulose and caustic hydrolyzed potato starch. In general the anionic aids worked best when particle charges (determined by electrophoretic mobility measurements) had been reduced to near zero with aluminium sulphate. The cationic aids were most efficient with low alum dosages. The eight aids used all could be made to improve or inhibit destabilization/floc formation by appropriate selection of dosages of alum and aid.

Mueller and Burbank(47), studying river turbidity removal with ferric sulphate, evaluated the use of three polyelectrolytes as flocculant aids: a nonionic, cationic and anionic polyelectrolyte (characteristics unspecified). Although, as for the work of Black and Hannah, all flocculant aids could give rise to improvements under appropriate conditions of metal coagulant and aid dosages, Mueller and Burbank found that the nonionic aid (probably a polyacrylamide) was the most effective in terms of settling rate and residual turbidity.

Black and Christman(9) applying flocculant aids to speed up floc formation during the lime-soda softening process, used four polyelectrolytes: activated silica, anionic polyacrylamide, nonionic potato starch and a cationic organic polyelectrolyte. As normal, for each of the aids a distinct optimum dosage was found. Each of the aids improved floc formation characteristics, although the anionic polyacrylamide appeared, from their results, to offer acceptable floc removal but at a much lower optimum dosage (0,025 mg l^{-1} as compared to approximately 1,0 mg l^{-1} for the other aids). Of interest is that with the nonionic (potato starch) aid, the addition of 17 mg l^{-1} aluminium sulphate as pre-coagulant had a marked detrimental effect on floc formation.

Huck <u>et al</u>(29) applied polyelectrolytes to aid flocculation of lime precipitated heavy metal (Fe, Zn, Cu, Mn, Pb) hydroxide flocs. The polyelectrolytes used had a molecular weight of $9{,}0.10^6$ (determined by gel permeation chromatography). Although the type of polyelectrolyte used by them appears to be unspecified, they found that the degree of hydrolysis, varied from 2 through to 37%, had no effect on flocculation. From their results, it appears that the optimum polyelectrolyte dosage is of the order 2.10^{-3} times the metal concentration. At the optimum dosage, the degree of floc formation and settleability were markedly improved.

Benedek and Bancsi(6) applied a wide variety of polyelectrolytes to evaluate the properties most appropriate when applied to phosphorus precipitated domestic wastewater using aluminium sulphate as primary coagulant. They found that, in opposition to normal manufacturers' recommendations of the highest hydrolysed polyelectrolyte species for alum precipitated phosphorus flocs, the polyelectrolyte giving the most superior results, in terms of floc formation and settling velocity, was an anionic polyacrylamide of molecular weight greater than $8,0.10^6$ and 10 to 20% hydrolysis. Under optimum conditions, overflow rates during primary sedimentation could be increased in some cases from approximately 0,75 $m\ h^{-1}$ with alum alone up to 7,0 $m\ h^{-1}$. The criterion used to monitor limiting overflow rate was 90% phosphorus removal. The aluminium dosage varied from 110 $mg\ l^{-1}$ to 190 $mg\ l^{-1}$.

5.4 POLYELECTROLYTES AS SLUDGE CONDITIONERS

Disposal of waste sludge from water or wastewater treatment plants is effected by a number of methods: with wastewater sludges, methods include a thickening stage and subsequently dewatering. Thickening is effected principally by gravity (sedimentation) or flotation and serves (in the absence of chemical conditioning) to remove free interstitial water only.

Dewatering of wastewater treatment sludges is effected by processes such as vacuum filters; filter pressing; filter belt pressing; centrifugation; drying beds and so on. Between the thickening and dewatering stages (or before these stages) biological sludges may be conditioned by aerobic or anaerobic digestion. In some cases, mechanical dewatering is carried out immediately after thickening without a biological conditioning stage.

Ultimate disposal of wastewater sludges is effected by simple techniques such as land irrigation (which may be unacceptable to many health authorities) and incorporation in composting plants (in which case thickening is probably essential; especially for secondary sludges) to sophisticated techniques such as incineration (multi-hearth furnaces, rotary hearth furnaces, fluidised bed furnaces, rotary drum furnaces), pyrolysis and so on.

Because of the relative fragility of biological flocs and the high degree of bound water, some form of chemical conditioning is required prior to relatively violent mechanical dewatering processes. Chemical conditioners include metal coagulants, such as aluminium chlorohydrate, ferric chloride, lime and copperas, and so on. Polyelectrolytes are now widely used as sludge conditioners because of their effectiveness in dewatering, the toughness of flocs produced and the fact that, unlike metal coagulants, they do not significantly add to the quantity of sludge to be ultimately disposed of. With biological wastewater treatment sludges, polyelectrolytes used are almost exclusively cationic, although this is not an unbroken rule.

With sludges from water treatment plants, a similar scheme of disposal is evident: Again, the thickening stage may include gravity sedimentation or flotation, possibly aided by chemical conditioners; and the dewatering stage includes processes such as belt filter presses; pressure filtration; vacuum filtration (rotary and horizontal); centrifugation (scroll and basket); sand bed drying and dual cell gravity solids concentration.

Other methods of treatment and disposal of water treatment plant sludges include acidic alum recovery; the freeze-thaw process; discharge to lagoons; landfill and disposal to sanitary sewers. In this latter case, in instances where chemical phosphorus removal is implemented in wastewater treatment plants, such discharge of waste alum sludge may be advantageous. Disposal of water treatment plant sludges is dealt with in greater detail in Appendix A.5.

As for wastewater treatment sludges, chemical conditioners are required for dewatering water treatment plant sludges. Again, with their inherent advantages, polyelectrolytes have been used with notable success. Here, there is no generality of the type of polyelectrolyte most effective since it depends very much on the type of raw water, its constituents, the primary coagulants and (if used) flocculant aids applied and so on. However, high molecular weight anionic polyelectrolytes with a moderate (15-30%) degree of hydrolysis have often proved to be most effective.

The evaluation of polyelectrolytes for dewatering facilities involves a determination of principally two parameters: filterability and floc strength. The experimental procedures are dealt with in Section 8.3.

As for preceding sections, the following presents a few selected examples to illustrate chemical conditioning of water and wastewater sludges with polyelectrolytes. As before, the examples are not by any means exhaustive.

Bratby(14), investigating thickening characteristics of activated sludge by dissolved-air flotation, found that applying a cationic polyacrylamide with a medium to high charge density (degree of hydrolysis 10-30%), molecular weight $10\text{-}12.10^7$ and at a concentration of 2g kg^{-1} TSS, found that for a given solids loading rate and height of float above the water level, float solids concentrations achieved were consistently higher (by a factor of 1,35) when compared to no polyelectrolyte addition. Furthermore, polyelectrolyte addition reduced the total depth of float solids thereby reducing the effective depth of unit required for thickening.

Effluent solids concentrations from the flotation unit were lower when using polyelectrolytes (mean value 6,7 mg l^{-1} compared to 37 mg l^{-1} with no polyelectrolyte addition). Bratby suggested that polyelectrolyte strengthened biological flocs were better able to resist break up within the relatively turbulent environment of the flotation unit.

Experiments carried out with a belt filter press, using the same sludge, identified the most effective polyelectrolyte in terms of aiding dewatering and prevention of clogging the belt fabric, to be the same as that used for flotation; however, the dosage required was higher (4g kg^{-1} dry solids).

For cases where flotation thickening precedes a dewatering facility (such as belt pressing), Bratby suggested that the advantage of polyelectrolyte usage is that since float solids concentration is increased (by a factor of 1,35), for a given set of operating conditions the volume of float solids to be handled by the dewatering facility (which governs the size of the facility) is concomitantly reduced. Presuming that the total polyelectrolyte dosage does not increase significantly a saving in total cost is achieved due to the reduced capital cost of the facility.

O'Brien and Novak(51) investigated the effects of pH and mixing on polyelectrolyte conditioning of chemical sludges (iron, iron-lime, alum and alum-lime) from several water treatment plants. From their studies, they suggest the following rules for initial polyelectrolyte selection: (i) cationic polyelectrolytes operate most efficiently at pH values of 7,0 or lower; (ii) nonionic polyelectrolytes and the lower percent hydrolysis anionic types function effectively over a pH range 6,5 to 8,5. In general, as the pH increased, effectiveness of polyelectrolytes decreased; (iii) a 50% hydrolysis anionic polyelectrolyte was most effective at pH values over 8,5. Below this pH value, its effectiveness correspondingly reduced; (iv) over or under-mixing reduces polyelectrolyte effectiveness greatly. The degree of mixing depends on the solids concentration of the sludge; the lower the solids concentration the longer is the optimum rapid mixing time.

Novak and Langford(50) investigated the use of polyelectrolytes for improving chemical sludge dewatering on sand beds. In their study a high molecular weight anionic polyelectrolyte was applied to various water treatment plant sludges. The sludges used were essentially the same as reported by O'Brien and Novak(51) above. They found that with polyelectrolyte conditioning, dewatering rates were greatly improved and bed penetration minimised.

Bratby and Marais(13), applying dissolved-air flotation to thicken sludge from a water plant treating humic coloured (brown) waters, used a cationic polyacrylamide (potable water grade) with a 10% degree of hydrolysis and molecular weight in excess of 7.10^6. The dosage applied was 0,5 g kg^{-1} dry solids. During treatment, humic substances were removed by 10 mg l^{-1} sodium aluminate followed by lime to adjust the pH to 5,5 after subsequent addition of 50 mg l^{-1} aluminium sulphate.

Because of the gelatinous nature of the flocs formed during the treatment process, the sludge concentration from the bottom of the sedimentation tanks never exceeded 2,5 g l^{-1}. With a polyelectrolyte conditioning and flotation combination, waste sludge was thickened to concentrations in excess of 120 g l^{-1}. That is, the volume of sludge to be ultimately disposed of is reduced by a factor of 50. Including polyelectrolyte conditioning at the particular plant would increase the overall chemical costs by a mere 1,43% of the existing chemical costs.

Bratby and Marais reported that without polyelectrolyte addition, although bubble-particle attachment did occur to a certain extent during flotation, the union was relatively short lived and, on the whole, the effluent was a very poor quality. A characteristic of alum precipitated brown humic water is the extreme fragility of the floc particles and a marked reluctance for reformation (within the time allowed during flotation) after being sheared apart by the relatively turbulent conditions created by precipitated bubbles in the flotation unit. Polyelectrolyte serves to considerably strengthen flocs and, after bubble-particle attachment, to resist dislodgement by shearing.

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6

Rapid Mixing

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6.0 INTRODUCTION

Rapid mixing refers to that stage in the overall coagulation-flocculation process where coagulant chemicals are added into the stream to be treated. The function of rapid mixing should not be considered to be one merely of efficient coagulant dispersion. The rapid mixing stage is possibly the most important operation in the process since it is here that destabilization reactions occur and where primary floc particles are formed, the characteristics of which markedly influence subsequent flocculation kinetics.

The importance of the efficiency of a rapid mixing facility is evident if the order of time of destabilization reactions is considered: The time for mononuclear complexes, such as $AlOH^{2+}$ and $FeOH^{2+}$, to form is of the order 10^{-10}s. Polynuclear complexes require from 10^{-2} to 1 s to form. The time required for adsorption of these species to particles is of the order 10^{-10}s(14). The time needed for adjusting the structure of the double layer is of the order 10^{-8}s and for a brownian collision (diffusion) of the order 10^{-7} to 10^{-3}s(15). The longest order of time scale is given by Overbeek(15) as the time required for charge adjustment at particle surfaces. This time may vary from as little as 10^{-6}s to as long as 10^{4}s.

From the above, it is appreciated that in many instances, traditional 30 to 60 s retention times during rapid mixing are unnecessary and that flocculation efficiency may not improve beyond rapid mix times of, say, 5 s(4). Indeed, beyond a certain optimum rapid mix time, a detrimental effect on flocculation efficiency may result(11). For a particular water and type of coagulant applied, the optimum retention time during rapid mixing is dependent on the velocity gradient and coagulant dosage applied.

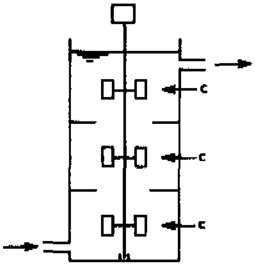
When carrying out coagulation tests in the laboratory, it will be found that optimum solids removal will be achieved by a particular combination of coagulant concentration and pH. The conditions of the laboratory experiments are such that complete and instantaneous dispersion of the coagulant chemicals into the sample of 'water' will be achieved readily (see Chapter 8). In practice, however, by applying the optimum coagulant dosage and pH as found in the laboratory, it is often found that the same degree of process efficiency cannot be achieved. This is largely due to an inadequate appraisal of the mode of destabilization necessary for the particular type of 'water' in question; and consequently the installation of a rapid mixing tank which cannot provide the requisite mixing environment.

6.1 REQUIREMENTS FOR RAPID MIXING DEVICES

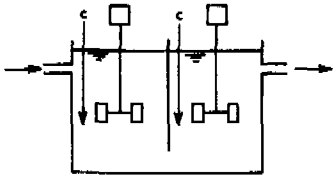
6.1.1 General

The types of rapid mixers most commonly installed in practice are represented schematically in Figure 6.1(19). Such mixers are given the general name *back-mix reactors* and usually are designed to provide a 10 - 60s retention time with a root mean square velocity gradient, G, of the order 300 s^{-1} (13). (Note that the concept of G is discussed in Chapter 7; see Section 7.2.1). In many instances where back-mix reactors have been installed for coagulant addition, they have been abandoned or not used extensively(17) due to the poor results often attained.

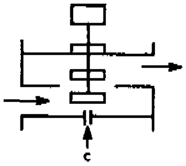
The basic characteristic (and in many instances, the shortcoming) of back - mix devices is that the particles within them have a distribution of residence times. That is, some of the particles will be short - circuited out almost immediately whereas some will stay in the reactor for longer periods than the nominal time. In the case of an adsorptive mechanism of destabilization using metal coagulants, this can be undesirable for the following reasons: (a) due to long residence times extensive hydrolysis of some of the applied metal coagulant to the relatively inefficient $Fe(OH)_3$ or $Al(OH)_3$ will take place and (b) poor overall destabilization of the particles will occur due to either incomplete adsorption or extensive adsorption of metal hydroxide species. What is needed is for the same (best) metal hydroxide species to be available to *every* particle simultaneously. A plug flow type of rapid mixer will be seen to approach this "ideal" situation the most satisfactorily since by virtue of its nature, all elements of liquid within it will theoretically have the same retention time.



a. Mechanical Mixer



b. Mechanical Mixer



c. In-Line Blender

FIGURE 6.1: Representative Types of Mechanical Agitation Devices Used for Rapid Mixing. (From Vrale and Jorden(19), with permission of the American Water Works Association).

For cases where an adsorptive mechanism of destabilization is not operative, Vrale and Jorden(19) presented the following considerations:

(a) If it is found that one needs to operate at say a $pH < 3$ with Al(III) or Fe(III) then a "Gouy-Chapman" type of destabilization will be effective and one will only need minimal rapid mixing since this type of destabilization is reversible(15).

(b) If an entrappment or 'sweep-floc' type of destabilization is found to be necessary then a back-mix reactor might be desirable since it has been found favourable for the formation of metal-hydroxide precipitates.

Furthermore, if one desires nucleation effects to take place, such as in the water-softening process or precipitation of phosphorus in tertiary biological processes, a back-mixer might also be desirable. However, some workers(3) suggest that use of back mix reactors in the latter instance may prove to be less efficient than the use of a plug flow type reactor.

(c) For sludge conditioning with, say, $FeCl_3$, excessive turbulence would lead to floc break-up and hence an increase in particle surface area - this indicates that a laminar flow type reactor would be best.

(d) For polyelectrolytes, where the method of destabilization is adsorptive in nature, then a plug flow facility, imparting a velocity gradient appropriate to the application, would be best.

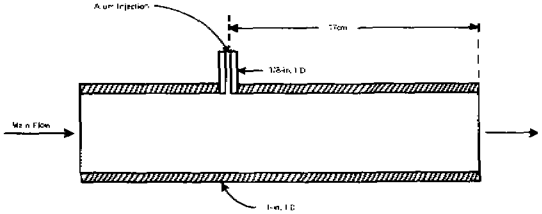
6.1.2 Comparison of Back-Mix and Plug-Flow Reactors

It is the objective of this section to present a quantitative comparison of the two basic types of rapid mix devices: back mix and plug flow reactors. Because of the very significant work carried out by Vrale and Jorden (19), this section essentially comprises a summary of their major findings. For a fuller account of the subject matter, the reader is referred to their paper.

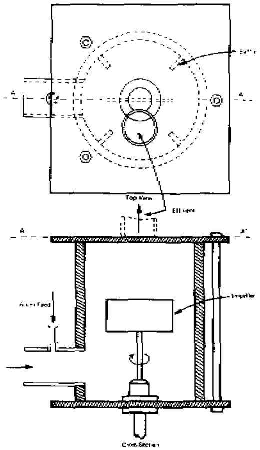
Vrale and Jorden, to investigate the most appropriate type of rapid mix unit and, with particular emphasis on an adsorptive mechanism of destabilization by metal - hydroxide species, devised the five rapid mix units shown in Figure 6.2:

Unit 1 was designed to investigate the mixing effect within a pipe.
Unit 2 was designed to simulate a 'back mix' reactor.
Unit 3 was selected because it had been proved elsewhere to afford a very rapid and high degree of mixing. It was intended that this unit should be the criterion for 'ultimate' rapid mixing.

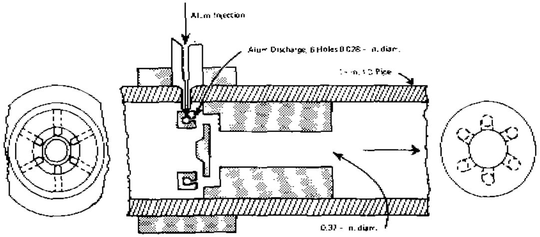
FIGURE 6.2: Rapid Mixers Used by Vrale and Jorden(19) (With Permission of the American Water Works Association).



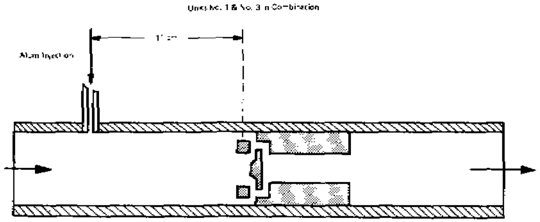
Cross Section of Rapid-Mix Unit No. 1



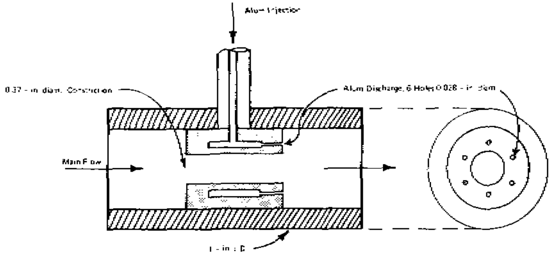
Rapid-Mix Unit No. 2



Rapid-Mix Unit No. 3. (Cross Section and Views Looking from Either End Are Shown)



Cross Section of Rapid-Mix Unit No. 4



Cross Section and End View of Rapid-Mix Unit No. 5

Unit 4 was designed as a combination of Units 1 and 3. It was employed in order to determine the effect of the time lag before intense mixing occurred.

Unit 5 was designed to simulate Unit 3 without the latter's impractical head loss and consequential shearing intensity.

The results obtained from their tests are illustrated in Figure 6.3 and the conclusions they came to with regard to the most efficient rapid mixing system are as follows: (Note: the criterion chosen for the efficiency of rapid mixing was the apparent aggregation rate K_{app} of the particles in a slow mix reactor - or flocculator

where $$\frac{1}{T_t} \approx \frac{1}{T_o} + K_{app}t \qquad (6.1)$$

and T_t = supernatant turbidity after time t of flocculation.

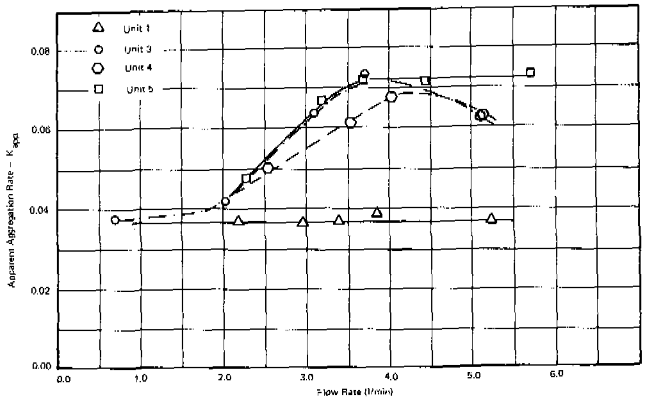
T_o = influent turbidity).

1. Unit 1 showed a constant rate of aggregation - *irrespective of the flow rate in the pipe.*

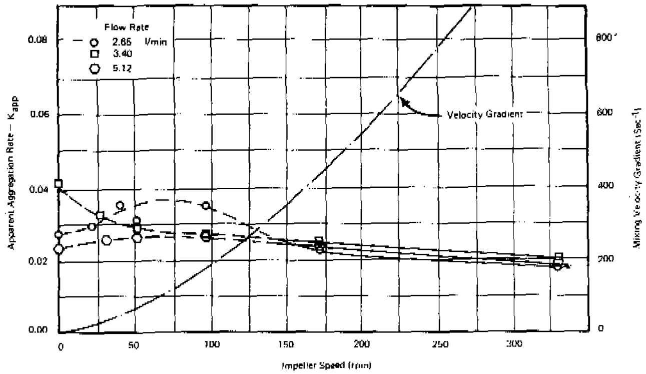
2. Unit 4 showed a marked increase in aggregation rate with increased flow rate, until at a certain flow rate, the rate of aggregation began to drop.

3. This drop in efficiency at higher flow rates was also evident in Unit 3. It was reasoned that because of the very high head loss (and consequent shearing intensity) in these two units, then at the higher flow rates break-up of the destabilized particles occurred.

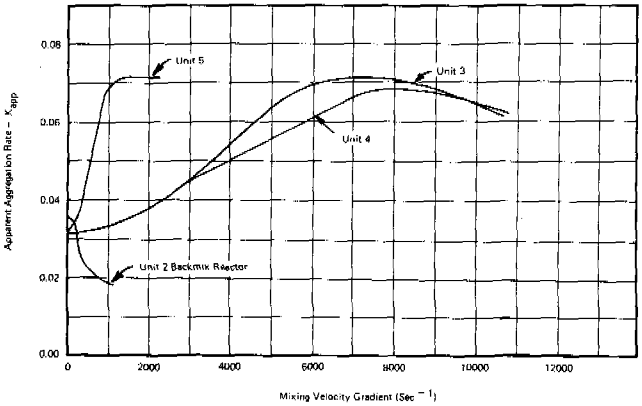
4. Unit 5 was found to give the best results since its efficiency reached a peak (similar to the peak in the 'next best' Unit 3) but did not decrease as did the others - it maintained a constant efficiency even at very high flow rates. The efficiency of Unit 5 reached a maximum when the hydraulic flow rate through the unit was increased to a value giving an average velocity gradient G of 1 200 sec^{-1}, thereafter remaining constant.



Aggregation Rate Results Versus Flow Rate for All Plug-Flow Reactors



Aggregation Rate Results Versus Impeller Speed for Rapid-Mix Unit No. 2, a Backmix Reactor



Aggregation Rate Results Versus Mixing Velocity Gradient for Rapid-Mix Units 2 through 5

FIGURE 6.3: Results Obtained Using Rapid Mixers Shown in Figure 6.2. (From Vrale and Jorden(19), With Permission of the American Water Works Association).

5. The results obtained for Unit 2, the back mix reactor (the type most commonly employed in present practice) indicate that this is the worst possible method of rapid mixing with a hydrolizing metal; increasing the impeller speed tended to decrease its efficiency and, conversely, at very low impeller speeds incomplete mixing was obtained.

From the above it is evident that a plug flow reactor, of a similar form to Vrale and Jorden's Unit 5 giving a velocity gradient of from 1 200 to 2 500 sec^{-1} should give optimum results when metal coagulants are used. As stated above, Vrale and Jorden suggested that Units 3 and 4 did not perform as well as Unit 5 because break-up of primary floc particles at higher flow rates had a detrimental effect on subsequent flocculation reactions. However, from Figure 6.3 it is evident that for Units 3 and 4, at a velocity gradient of 2 000 s^{-1} found optimal for Unit 5, the efficiencies of these two units were minimal. It would appear, therefore, that there are further factors to be considered besides excessive velocity gradients since efficiencies for Units 3 and 4 were maximal at velocity gradients as high as 7 500 sec^{-1}.

Even though the points of maximum shearing intensity (or velocity gradient) occurred at the plates, it is evident that the lower velocity gradient at the point of expansion is the most effective with respect to rapid mixing efficiency. There are two possible reasons: firstly the liquid velocity in the system is a maximum at the plates and through the constriction such that the residence time is minimal. Secondly, even though there is a high shearing intensity at the plate, the flow is fairly uniform being at a point of contraction. Effective mixing only occurs at the point of expansion where turbulent eddies are set up. This argument is supported by Vrale and Jorden's data where maximum efficiencies for all three Units 3 to 5 occur at approximately the same flow rate. The head loss, h_L, at the point of expansion must be the same in each case whereas the overall head loss for Units 3 and 4 is far greater. (Note that velocity gradient, G, is proportional to $h_L^{1/2}$; see Section 7.3.2.1).

6.1.3 Velocity Gradient Requirements

The work of Vrale and Jorden, outlined above, is especially useful in identifying the fact that a high velocity gradient alone is not sufficient guarantee that efficient rapid mixing is achieved. The scale and intensity of the turbulence at the point of coagulant addition probably has more significance (see also Section 7.2.1).

Although some workers point out the desirability of intense rapid mixing (i.e. high G values) to maximise efficient use of coagulant(3), there is an upper limit for a particular application. Camp(1) showed that too high velocity gradients during rapid mixing can delay floc formation during subsequent flocculation. The delay time depends on the velocity gradient applied: using a G of 12 500 s^{-1}, no floc was visible up to a 45 minute flocculation period. With G = 4 400 s^{-1} pinpoint floc was observed after 10 minutes flocculation. However, of significance is that if rapid mixing was performed at a G of 1000 s^{-1}, then subjected to a G of 12 500 s^{-1} and then flocculated, flocs formed successfully and were visible after 18 minutes flocculation. This emphasises further the importance of a correct rapid mixing procedure, the success of which influences strongly the efficiency of downstream processes.

In the light of previous comments pointing out the inadequacy of the r.m.s. velocity gradient, G, in characterizing a rapid mix facility, it is difficult to set down design guidelines. However, if one takes pertinent examples and appreciates the configuration of the particular rapid mix device, reasonable indications may be obtained. With an in-line rapid mix (plug flow) unit, using a hydrolyzing metal coagulant, the range of appropriate G values appears to be from 1200 to 2500 s^{-1}(19). Using a back-mix reactor for the same application the efficiency appears to decrease as G values are increased from near zero(19).

Using cationic polyelectrolytes as primary coagulants in the treatment of a turbid water, Morrow and

Rausch(13) recommend the use of G values between 400 to 1000 s^{-1}. These workers point out that the reported failure, in many instances, of polyelectrolytes used as primary coagulants may be due to inadequate velocity gradients being applied at the rapid mix stage. However, too high velocity gradients (> 1000 s^{-1}) may give rise to primary floc break-up and "armouring" of the flocs with polyelectrolyte segments, thus effectively inhibiting further flocculation. Of interest in their work is that if rapid mixing occurs for too long a period (over 1 to 2 minutes) or, if high G values are reduced too rapidly, floc formation is inhibited during subsequent flocculation.

6.1.4 Rapid Mixer Retention Time

It was implied above that rapid mixing for extended periods may give rise to a deleterious effect during subsequent flocculation. For a particular application there does in fact appear to be an optimum rapid mix period for which the rate of flocculation is maximised. This time appears to be principally a function of rapid mix velocity gradient and metal coagulant concentration. The higher the coagulant concentration and the higher the velocity gradient the lower in general is the required rapid mix period. In a study by Letterman _et al_(11) the optimum rapid mix period (G = 1000 s^{-1}) ranged from 9 seconds to 2,5 minutes for alum concentrations ranging from 100 to 10 mg l^{-1} respectively. In contrast, other workers(4) found that turbidity removal, after flocculation and settling, was not influenced by rapid mix detention period (5 to 60 seconds) even though the velocity gradient applied was relatively low (350 s^{-1}).

From the above, choice of a suitable rapid mix period to be used for design is somewhat complicated. For surety in final design, laboratory scale and/or pilot scale studies need to be conducted using the particular water under test.

6.1.5 Tapered Rapid Mix Velocity Gradient

With coagulation - flocculation facilities there is often an interruption of up to several minutes from the high velocity gradients during rapid mixing to the low velocity gradients during flocculation. The only intermediate mixing in such instances arises from the velocity gradients existing within the connecting conduit or channel. Intermediate G values in these cases are determined from the head loss along the conduit or channel.

A sharp decline in velocity gradient (from, say, 1000 down to 100 s^{-1}) can have a detrimental effect on subsequent (final) water quality. By striving to maintain a given final water quality, coagulant dosages with interrupted mixing may be as high as 30 to 40 per cent greater than if tapered rapid mixing is provided(10). Morrow and Rausch(13), using cationic polyelectrolytes as primary coagulants, found that if rapid mix velocity gradients were suddenly lowered to low velocity gradients of from 5 to 100 s^{-1} during flocculation, small flocs formed which neither grew nor settled during and after flocculation. This effect was not evident if tapered rapid mixing was employed to lower velocity gradients gradually. It should be noted that a tapered velocity gradient profile is also beneficial during flocculation: see Section 7.3.4.

6.1.6 Coagulant Feed Concentration

Several workers have reported the effect of the concentration of coagulant solution fed to the rapid mix unit(4, 7, 8, 9, 10). Too high a concentration for a given rapid mix device may result in poor water quality after flocculation and solid-liquid separation. When mixing a small flow of coagulant solution with a much larger stream of raw water, dilute coagulant solutions disperse more rapidly and uniformly than concentrated solutions. Kawamura (9) found that dilution of stock alum solution, in the case of turbidity removal, to within the range 0,5 to 5% resulted in high residual turbidities. Coagulant feed concentrations less than 0,5% or greater than 5% resulted in the lowest (optimal) residual turbidities. It is difficult to explain this apparent anomaly. The unusual jar testing procedure used by Kawamura may have had an effect (he placed the alum dosage into the sample jar and then added the water sample, agitating the contents by hand) but if the same procedure was followed for the whole series it is likely that the trend of the results are reliable. In a later paper, Kawamura(10) recommends an alum solution concentration of the order 0,5% fed to the rapid mixer. This concentration has also been suggested by other workers(4). However, too low coagulant solutions (< 0,1%(7) to 0,3%(4)) may result in poor performance due to pre-hydrolysis of metal species before addition to the raw water stream.

On the subject of coagulant addition, it should be noted that in cases where alkaline reagent (e.g. lime) or acid needs to be added with the coagulant to adjust raw water pH to the optimum final pH for that particular water, such chemicals must be added *before* or in some cases at the *same* time as the coagulant. It should not be added after coagulant addition since destabilization reactions which commence at the time of coagulant addition are not necessarily reversible.

With polyelectrolytes, the feed concentration is usually dictated by manufacturers' recommendations. However, as a rough guide solid grade products are normally recommended to be within the range 0,02 to 0,1% and, with liquid grade products, dilution to 100:1 is often recommended. Stock solution concentrations of solid grade products are normally made up with viscosities of the order 500 cps; Higher solution concentrations present handling problems due to the correspondingly higher viscosities. Commonly recommended stock solution concentrations are of the order 0,2 to 0,5%.

Multiple point addition is often recommended when dosing polyelectrolytes to the water/wastewater stream to be treated. As stated in Section 5.1.2.3 such a procedure probably assists the bridging mechanism of destabilization by retaining *loops* for a sufficient period. A further benefit is that inadequate rapid mixing may to a certain extent be overcome. However, from preceeding discussions, it would appear to be preferable to design a rapid mixing facility with polyelectrolyte addition at one point only provided that a suitable velocity gradient is applied appropriate to the application. In any case, multiple point addition can usually be instituted at a later stage if conditions warrant such a procedure.

6.2 DESIGN OF RAPID MIXING DEVICES

6.2.1 General

There are several types of rapid mixing devices which may be installed in a given coagulation-flocculation process system. Essentially they may be subdivided into three principal groups: back mix reactors; partial back mix reactors and plug-flow in-line reactors.

When designing a rapid-mixing facility, a difficulty arises when different flow rates are to be catered for. As pointed out in an earlier section, for a particular water, coagulant type, dosage and rapid mix device, there is associated a particular value of velocity gradient, G, which produces best results. With rapid mix devices relying on hydraulic considerations alone, this optimal G value may be difficult to maintain at different flow rates. With rapid mixers relying on impellers to produce velocity gradients, the situation is simplified since an adjustable rotational speed to the impeller can serve to maintain the required intensity of mixing. However, as discussed earlier, such mixers fall into the back-mix or partial back-mix category and, therefore, for most cases do not produce the appropriate mixing environment.

This section discusses the design of several specific rapid mix devices. In several instances it is difficult to categorise whether a particular device may be described as a partial-backmix type or a true plugflow type. For the purposes of this section, therefore, rapid mixers will be categorised as back-mix reactors, in line reactors where velocity gradients are variable and fixed G in line reactors. Bearing in mind the discussions of preceeding sections, the following should, it is hoped, serve as a preliminary guide in choosing an appropriate device for a particular system.

6.2.2 Backmix Reactors

The configuration of backmix reactors was schematically presented earlier. Figure 6.4 shows a typical installation using a single impeller. As stated previously there are a few instances (e.g. in the lime-soda softening process) where a back-mix reactor may be suitable. However, for most applications indications are that a plug flow type system is best. With installations such as Figure 6.4, the shear gradients applied may be adjusted to cater for varying flow rates by varying the speed of rotation of the impeller. Since velocity gradients produced by such proprietary equipment depend very much on the type of impeller, design is best carried out using data supplied, or left to the manufacturer.

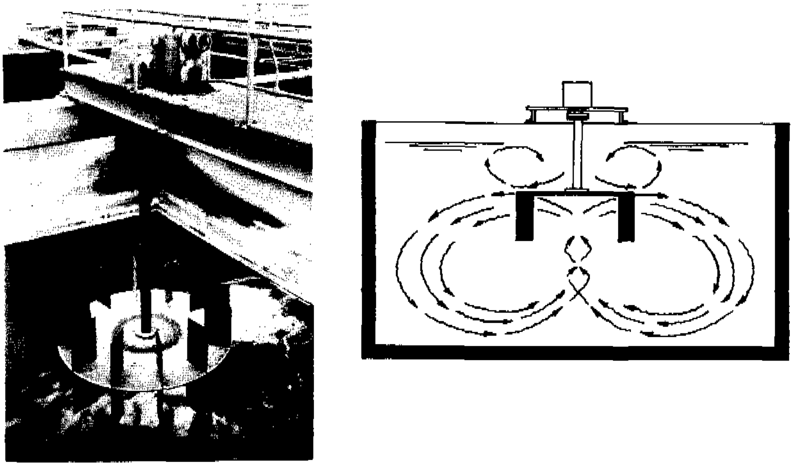


FIGURE 6.4: Typical Back-Mix Type Rapid Mixing Installation. (Infilco VORTI Mixer, Courtesy Westinghouse Electric Corp.).

6.2.3 In-Line Mixers With Varying Velocity Gradient Facility

Two examples of such rapid mix devices are shown in Figures 6.5 (a) and (b) respectively. The first shows a device recommended by Kawamura(10), where the effective velocity gradient is determined by the discharge rate through the nozzle. Design is based on the following:

From Section 7.2.1, velocity gradient G is given by $G = (W/\mu)^{1/2}$ where μ = absolute viscosity of liquid (for water = 10^{-3} N s m^{-2} at 20°C). W, the dissipation function, is given by power dissipated, P, divided by volume. P is given by

$$P = \frac{C_{d}.av^{3}\gamma}{2g} \qquad (6.2)$$

where C_d = discharge coefficient of orifice ($\pm$ 0,75);

a = area of orifice (m^2);

v = velocity of flow through orifice ($m\ s^{-1}$);

γ = unit weight of liquid ($=9{,}81.10^3\ N\ m^{-3}$);

g = weight per unit mass on earth's surface ($=9{,}81\ N\ kg^{-1}$).

Hence W = P/V where V is the volume of influent pipe over which rapid mixing is effective. From Kawamura's data it appears that V may be estimated from the spray cone angle and diameter d (m) of influent pipe, i.e. $V = 0{,}33\ d^3\ m^3$.

Hence $W = P/(0{,}33\ d^3)$ and

$$G = \left(\frac{P}{0{,}33d^{3}\mu}\right)^{1/2} \quad s^{-1} \qquad (6.3)$$

As an example, referring to Figure 6.5 (a), Kawamura gives for a flow of 3,6 $m^3\ s^{-1}$, a jet velocity of 7,3 $m\ s^{-1}$ *and a 60 l* s^{-1} *coagulant dosage rate, a G value* of 1000 s^{-1}.

From a consideration of Equations (6.2) and (6.3) it is seen that the design velocity gradient, G, may be maintained at varying flow rates during operation by varying the coagulant dosage feed rate through the nozzle. This may be accomplished by a variable flow dosing pump or, a number of dosing pumps and a number of coagulant dissolution/holding tanks, etc.

The second in-line mixer with a varying velocity gradient facility, shown in Figure 6.5 (b), is an example of proprietary devices available. Such devices may be equipped with variable speed drives thus catering for different flow rates. Design here is essentially left to the manufacturer.

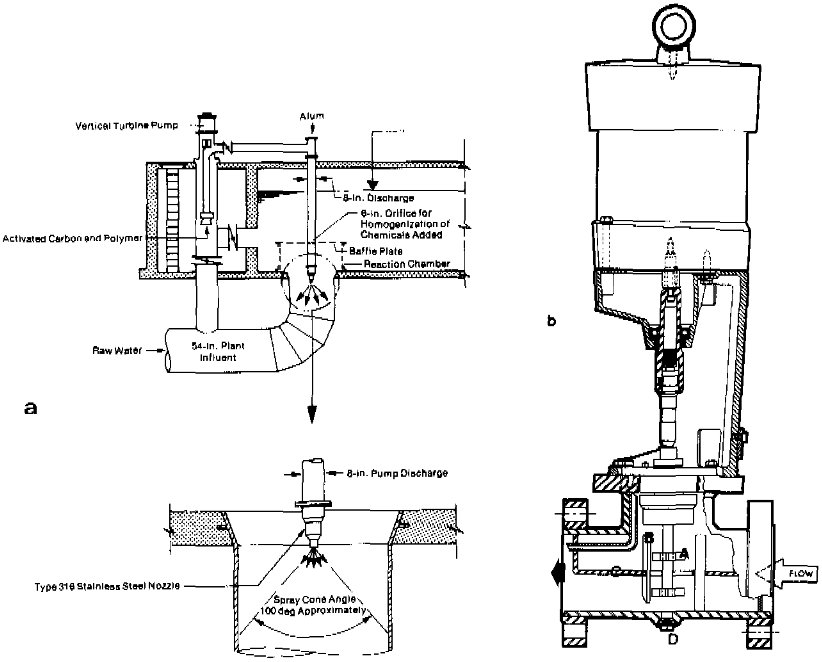


FIGURE 6.5: Examples of In-Line Mixers With Varying Velocity Gradient Facility; (a) from Kawamura(10) (With The Permission of the American Water Works Association); (b) *Lightnin* in-line mixer: A = radial flow impellers; B = baffles; C = separator plate; D = auxiliary inlet and/or drain (Courtesy *Lightnin*).

6.2.4 Fixed Velocity Gradient In-Line Rapid Mixers

There are a number of hydraulic appurtenances which may be considered in this category(16). Those dealt with here are pipe bends; sudden expansion within a pipe; orifice plate within a pipe and hydraulic jump in channel flow. For each of the following the average velocity gradient is as given in Section 7.3.2.1, i.e. $G = (\gamma . h_f / T\mu)^{1/2}$ where γ and μ are as given above; h_f = head lost due to friction (m) and T is the retention time (seconds).

6.2.4.1 Pipe Bend

In computing the head loss across a pipe bend it is convenient to convert the bend to an equivalent length of straight pipe. Figure 6.6 taken from

Ziemke(20) shows the total resistance to flow in 90° bends or elbows characterised by the ratio radius of curvature of bend to diameter of pipe. The resistance to flow is in terms of the equivalent length of straight pipe in pipe diameters. For a number of 90° bends in series, an approximation to the total head loss is given by the sum of the head losses for each bend(20). For the case of a 45° bend, the head loss is given by 0,4 times the head loss for a 90° bend(6).

For computing average velocity gradient, G, from the head loss, an assumption as to the effective mixing length has to be made in order to compute retention time. Although the flow pattern is only completely re-established 50 to 100 diameters downstream of the bend, 80% of head loss occurs within 5 diameters(6). It is reasonable, therefore, to adopt this latter length for determining mixing retention time(16).

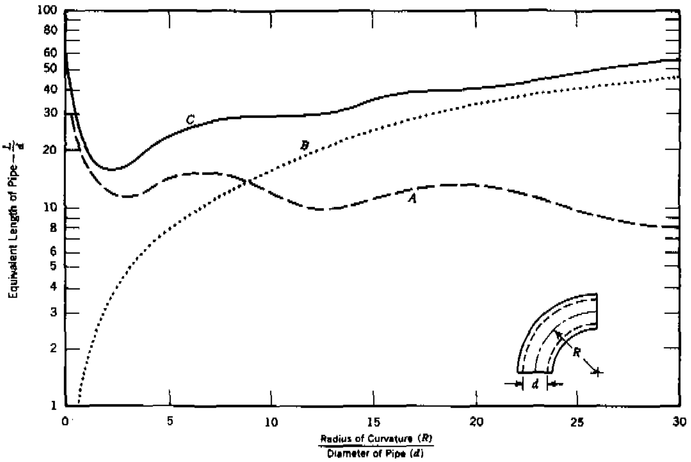


FIGURE 6.6: Resistance to Flow in Pipe Bends and Elbows; Curve A-resistance due to curvature; Curve B-resistance due to pipe length; Curve C-total resistance in 90-deg bend (From Ziemke(20), With Permission of the American Water Works Association).

To give a comparative example, the same figures as used previously in Section 6.2.3 will be used here. Again, a rapid mix velocity gradient, G, of 1000 s^{-1} is required; the influent pipe has a diameter, d, of 1,37 m and the flow, Q, is 3,6m^3 s^{-1}. The required head loss is given by a rearrangement of the equation $G = (\gamma\ h_f/T\mu)^{1/2}$.

i.e. $h_f = G^2\ T\mu/\gamma = T/9{,}81$ m (6,4)

Head loss in a straight length of pipe is given by(5):

(a) For extremely smooth pipes: $h_f = 0{,}54.10^{-3}Lv^{1{,}75}/d^{1{,}25}$. (6.5).

(b) For fairly smooth pipes : $h_f = 0{,}78.10^{-3}Lv^{1{,}86}/d^{1{,}25}$. (6.6).

(c) For rough pipes : $h_f = 1{,}15.10^{-3}Lv^{1{,}95}/D^{1{,}25}$. (6.7)

(d) For extremely rough pipes: $h_f = 1{,}68.10^{-3}Lv^2/d^{1{,}25}$ (6.8).

where L = (equivalent) length of straight pipe (m);
v = average velocity of flow, Q/A (m s^{-1}) and
d = diameter of pipe (m).

For the present example, assuming a fairly smooth pipe, $h_f = 2{,}77.10^{-3}L$.

Retention time, T, during mixing = total mixing volume)/(flow) = $\frac{\pi\ d^2}{4}\ (n\ \frac{\pi\ R}{2} + 5d)/Q = 0{,}41\ (1{,}57\ nR +$

$+\ 6{,}85)$

where n = number of bends or elbows in series and 5d = mixing length in straight pipe section after (series of) bend(s).

From Figure 6.6, taking the lowest practicable R/d ratio of 0,5 (sharp elbow), the equivalent length of straight pipe per elbow, L/d = 30 i.e. L = 41,1 m

Hence $h_f = 2{,}77.10^{-3}.41{,}1 = 0{,}114$ m per elbow.

From Equation (6.4), required $h_f = T/9{,}81 =$

$$= \frac{0{,}41}{9{,}81}\ (1{,}57nR+6{,}85)$$

For R/d = 0,5 (i.e. R = 0,69) the number of elbows in series is given by

$$0{,}114n = \frac{0{,}41}{9{,}81}\ (1{,}57n0{,}69 + 6{,}85)$$

from which n = 4,17 (= ± 4).

Hence, for the present example, one may install the equivalent of an expansion U bend, comprising four elbows in series with a radius of curvature 0,69m, as shown in Figure 6.7 (a).

6.2.4.2 Sudden Expansion Within a Pipe

At a sudden expansion in a pipe, a backwash of eddies will be formed at the corner of the enlargement giving rise to a loss of head. The magnitude of the head loss is derived from Bernoulli's equation and is given by

$$h_L = \frac{(v_1 - v_2)^2}{2g} \qquad (6.9)$$

where v_1 = velocity of flow before enlargement (m s^{-1})

and v_2 = velocity of flow after enlargement (m s^{-1}).

Using the same example as given above, the diameter of the constricted flow to produce a G value of 1000 s^{-1} on sudden re-expansion to a diameter of 1,37 m (see Figure 6.7 b) is computed as follows:

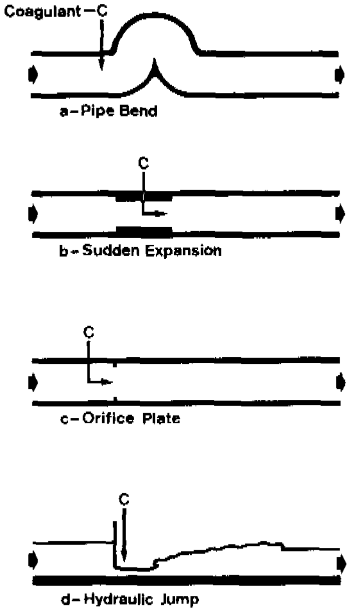


FIGURE 6.7: Fixed Velocity Gradient In-Line Rapid Mixers

From Equation (6.4):

$$h_L = G^2 \, T \, \mu/\gamma = T/9{,}81 \text{ m.}$$

Assuming that most of the head loss occurs within 5 diameters from the expansion, T is given by

$$T = \left(\frac{\pi \, d_2^2}{4} \cdot 5d_2\right)/Q = 2{,}8 \text{ s,}$$

where d_2 is the diameter of pipe downstream of the enlargement. Hence, required head loss, $h_L = 2{,}8/9{,}81 = 0{,}29$ m

Diameter of constricted section given by a re-arrangement of Equation (6.9):

$$d_1 = \left(\frac{4Q}{\pi} \cdot \frac{1}{(2gh_L)^{1/2} + v_2}\right)^{1/2} = 0{,}97 \text{ m}$$

The form of the rapid mix unit for the above example is shown in Figure 6.7 b.

6.2.4.3 Orifice Plate Within a Pipe

Head loss within a pipe may be induced by situating an orifice plate at the point desired for mixing. The magnitude of the head loss at an orifice in pipe flow is given by(18):

$$h_L = K\ v^2/2g \qquad (6.10)$$

where $K = 2{,}8(1 - \beta^2)\ \{\ (1/\beta)^4 - 1\ \}$ (6.11)

and β = ratio diameter orifice/diameter pipe.

As before, for the above example, h_L required = T/9,81 m. Assuming once again that mixing persists for five diameters downstream of the orifice, h_L required = 0,29 m.

From Equation (6.10), $K = 2g\ h_L/v^2 = 0{,}96$

Hence $(1-\beta^2)\ \{(1/\beta)^4 - 1\} = 0{,}34$.

from which $\beta = 0{,}83$.

Hence diameter orifice = 0,83.1,37 = 1,14 m.

The form of the orifice plate used as a rapid mixer within a pipe for the above example is illustrated in Figure 6.7 c.

6.2.4.4 Hydraulic Jump in Channel

Hydraulic jumps in open channel flow have been used extensively and for no little time(12) as mixing devices in water/wastewater treatment plants. In many instances a hydraulic jump formed downstream of a flow measuring flume has been used for mixing chemicals but the mixing intensity achieved here is a case of serendipity.

There are several methods by which a hydraulic jump may be induced to form. These include (a) altering floor slope, (b) narrowing the channel and (c) including a sluice gate. From the point of view of facilitating control, method (c) is probably preferable(16).

Hydraulic jumps on horizontal floors are of several distinct types and can be classified according to Froude number, F_1, of the incoming flow(2):

For $F_1 = 1$, the flow is critical and hence no jump can form.

For $F_1 = 1$ to $1,7$, the water surface shows undulations and the jump is called an "undular jump".

For $F_1 = 1,7$ to $2,5$ a series of small rollers develop on the surface of the jump, but the downstream water surface remains smooth. The velocity throughout is fairly uniform and energy loss low. This jump is called a "weak jump".

For $F_1 = 2,5$ to $4,5$, there is an oscillating jet entering the jump bottom to surface and back again with no periodicity. This jump is called an "oscillating jump".

For $F_1 = 4,5$ to $9,0$ the downstream extremity of the surface roller and the point at which the high velocity jet tends to leave the flow occur at practically the same vertical section. The action and position of this jump are least sensitive to variation in tailwater depth. This jump is called a "steady jump".

For $F_1 > 9,0$, the high velocity jet grabs intermittent slugs of water rolling down the front face of the jump generating waves downstream and a rough surface can prevail. This jump is called a "strong jump".

A hydraulic jump will form in a channel if the Froude number F_1 of the approach flow, the approach flow depth, y_1 and the downstream depth, y_2 satisfy the equation

$$\frac{y_2}{y_1} = 1/2 \left(\sqrt{1 + 8F_1^2} - 1 \right) \qquad (6.12)$$

where $F_1 = v_1/(gy_1)^{1/2}$ (6.13)

and v_1 = approach velocity (m s^{-1}).

The loss of energy in the jump is given by

$$h_L = \frac{(y_2 - y_1)^3}{4\, y_1 y_2} \text{ (m)} \qquad (6.14)$$

The length of the jump, L, is given as a function of Froude number and expressed as the ratio L/y_2. Chow(2) presents empirical data as shown in Figure 6.8 .

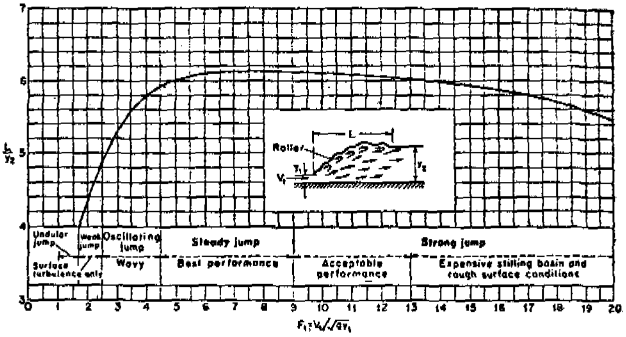


FIGURE 6.8: Length in Terms of Sequent Depth y_2 of Jumps in Horizontal Channels (From Chow (2), With Permission of McGraw-Hill).

For comparative purposes the following example is based on the same figures used previously i.e. a required G value of 1000 s^{-1} and a flow of 3,6 m^3 s^{-1}. There are a number of possible alternatives depending on the channel dimensions chosen. For example, for a channel width of 2,5 m and an approach upstream velocity of 1,2 ms^{-1} (upstream head = 1,2 m), by trial and error the appropriate depth under the sluice gate is found to be 0,34 m, viz:

Velocity under the gate, v_1 = 4,24 m s^{-1}

Froude number, F_1 = 2,32 (i.e. a weak jump)

Depth downstream of jump, $y_2 = \frac{y_1}{2} (\sqrt{1+8F_1^2} - 1) = 0{,}96$ m

Velocity downstream of jump, v_2 = 1,5 m s^{-1}

Head loss across jump $= \frac{(y_2 - y_1)^3}{4\, y_1 y_2} = 0{,}18$ m

Length of jump (from Figure 6.8) = 4,56 m

Mixing time = (length of jump)/(average velocity through jump)

$$= 4{,}56/ \frac{(v_1 + v_2)}{2} = 4{,}56/ \frac{(4{,}24 + 1{,}5)}{2} = 1{,}59 \text{ s}$$

Hence average velocity gradient, $G = \left(\frac{9{,}81.10^6.0{,}18}{1{,}59}\right)^{1/2}$

$= 1050\ s^{-1}$.

Dimensions of the jump are shown in Figure 6.7 (d).

Although the jump as calculated above for a G of 1000 s^{-1} will only form in the channel for the flow rate of 3,6 m^3 s^{-1}, higher and lower flow rates may be catered for by installing an adjustable control (sharp crested) weir downstream of the jump$^{(2)}$.

6.2.4.5 *Discussion of Fixed Velocity Gradient In-Line Rapid Mixers*

The above sections presented four alternatives for in-line rapid mixers where the average velocity gradient is fixed for a given flow. The alternatives chosen are by no means exhaustive but, it is hoped, serve as a representative indication of practicable methods of producing requiring average velocity gradients.

The shortcoming of each of the above methods is that for a given pre-determined average velocity gradient there is only one flow rate through the rapid mix device which will produce the required head loss. With certain provisions, an exception is the use of the hydraulic jump. By providing a calibrated adjustable sluice gate and sharp crested weir upstream and downstream of the jump respectively, it should be possible to design for the expected range in flow rates through the plant. A prerequisite, however, is that the average velocity gradient produced after the hydraulic jump (i.e. over the control weir) does not disrupt primary floc formation. However, it was stated previously that a tapered rapid mix velocity gradient profile is preferable to an abrupt drop from the high shear intensity at the rapid mix device to that existing in the channel or pipe. Therefore, it would seem that elevated velocity gradients set up at the control weir may well aid rather than deter from the efficiency of the process. In the case of post flocculant aid addition, the existence of such a secondary rapid-mix device may be an advantage.

In the light of the above comments, one can suggest a means by which varying flow rates can be accomodated using hydraulic appurtenances producing a fixed head loss:

Installing a number of similar units, each successive unit producing progressively less head loss, one can approximately maintain a given average velocity gradient at the point of coagulant addition by appropriately diverting the coagulant feed to that unit giving the required loss for a particular flow rate. The first unit in the series will be sized according to the lowest expected flow and the last according to the highest. At times when the flow is less than maximum, downstream units will provide a tapered velocity gradient profile. Furthermore, where floccculant aids need to be added downstream of primary coagulant addition (usually at a lesser velocity gradient) a suitable system of feed pipes and control valves will allow the operator to change feeds to the appropriate points.

6.2.4.6 Example

An in-line rapid mixing facility is to be designed for a 2m diameter pipe line. For the particular water, the following criteria are optimal: Addition of aluminium sulphate at a concentration of 50 mg l^{-1} and at an average velocity gradient of 1200 s^{-1} with a minimum rapid mix time of 5 s; followed by polyelectrolyte addition at a concentration of 0,25 mg l^{-1} with an average velocity gradient of 350 s^{-1}. After polyelectrolyte addition the average velocity gradient is to be reduced gradually to that existing in the pipe. The minimum and maximum expected flows to the treatment plant are 3,0 $m^3\ s^{-1}$ and 8 $m^3\ s^{-1}$ respectively. Design should provide flexibility such that within the range of expected flows, the above criteria are reasonably satisfied.

It is considered, for this design, that a series of orifice plates within the pipe offer the simplest solution. Design is carried out using the principles set down in Section 6.2.4.3. A satisfactory methodology followed for the calculations is as follows:

(i) Take a series of, say, six equal increments of flow between the minimum and maximum. For the average of the lowest increment (ranging from the minimum flow to one - sixth the difference between minimum and maximum plus the minimum flow) determine the size of orifice plate required for a G of 1200 s^{-1}.

(ii) For the average of the highest increment of flow, determine the size of orifice for G = 1200 s^{-1}.

(iii) Again, for the smallest increment, determine the size of orifice required for a G of 350 s^{-1}.

(iv) For the highest increment, determine the size of orifice for a G of 350 s^{-1}.

(v) For each of the four orifices as calculated above, determine the range of G values for each increment of flow. From this it can be judged whether, by suitably manipulating control valves, a reasonably consistent rapid mixing regime may be maintained at all flows.

Table 6.1 shows that for this example, four orifice plates are provided with successive diameters 1,06; 1,54; 1,63 and 1,84m respectively from the upstream end. Successive distances between the orifices are 6,1m; 8,75m and 4,0m respectively.

FLOW $m^3 s^{-1}$	ALUM ADDED TO ORIFICE *	POLY. ADDED TO ORIFICE *	DISTANCE BETWEEN ORIFICES m	RAPID MIX TIME FOR ALUM s
3,0-3,8	A 1004 to 1460 1,06	B 300 to 437 1,54	6,10	6,42-5,0
3,8-4,7	A 1460 to 1952 1,06	C 318 to 424 1,63	14,85	12,17-10,0
4,7-5,5	B 584 to 750 1,54	C 424 to 545 1,63	8,75	5,91-5,0
5,5-8,0	B 750 to 1320 1,54	D 214 to 375 1,84	12,75	7,29-5,0

*

Orifice Designation (see Fig.6.9)	Range of G values s^{-1}
Diameter m	

TABLE 6.1

For flows between 3,0 and 4,7 $m^3\ s^{-1}$ alum should be added at orifice A and from 4,7 to 8,0 $m^3\ s^{-1}$ to orifice B. For flows between 3 and 3,8 $m^3\ s^{-1}$ polyelectrolyte should be added to orifice B, from 3,8 to 5,5 $m^3\ s^{-1}$ to orifice C and from 5,5 to 8,0 $m^3\ s^{-1}$ to orifice D.

Rapid mix times from the point of alum addition to polyelectrolyte addition range from 5 to 12 seconds. Average velocity gradients for alum addition range from 584 to 1952 s^{-1} and for polyelectrolyte addition from 214 to 545 s^{-1}.

In this example, the velocity gradient in the pipe downstream of the orifice plates ranges from 53 s^{-1} at minimum flow to 216 s^{-1} at maximum flow. At minimum flow the velocity gradient profile through the orifices (from the point of alum addition), is 1004 - 300 - 218 - 85 - 53 → s^{-1}, and at maximum flow 1320 - 960 - 375 - 216 → s^{-1}.

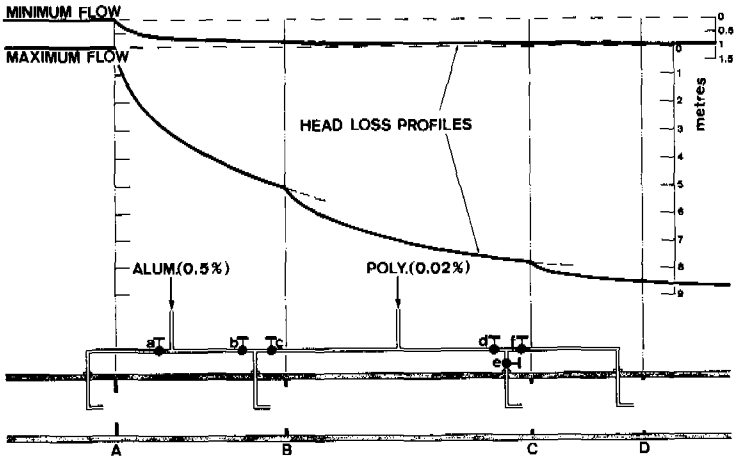


FIGURE 6.9: Scheme of the Rapid Mixing Facility For Example; Showing a Possible Layout of Alum and Polyelectrolyte Feed Pipes and the Head Loss Profiles Through the Facility at Minimum and Maximum Flows Respectively.

Figure 6.9 shows the scheme of the rapid mix facility, a possible layout of alum and polyelectrolyte feed pipes and the head loss profiles through the facility at minimum and maximum flows respectively.

For the present example, assuming an aluminium sulphate feed concentration of 0,5% and a polyelectrolyte feed concentration of 0,02%, a possible set of operator instructions, referring to Figure 6.9, could be as listed in Table 6.2.

Although the above example was based on orifice plates to produce elevated velocity gradients within a pipe, there is no intended implication that the use of other hydraulic appurtenances is precluded. The general idea of maintaining within certain limits a desired intensity of mixing and, at the same time, providing a tapered velocity gradient profile under varying flow conditions is equally applicable to other methods of producing elevated velocity gradients.

FLOW $m^3 s^{-1}$	ALUM FEED RATE $l s^{-1}$	POLYELECTROLYTE FEED RATE $l s^{-1}$	VALVES TO BE OPEN *	VALVES TO BE CLOSED *
3,0	30	3,75	a,c	b,d
3,5	35	4,38	a,c	b,d
4,0	40	5,0	a,d,e	b,c,f
4,5	45	5,63	a,d,e	b,c,f
5,0	50	6,25	b,d,e	a,c,f
5.5	55	6,88	b,d,e	a,c,f
6,0	60	7,50	b,d,f	a,c,e
6,5	65	8,13	b,d,f	a,c,e
7,0	70	8,75	b,d,f	a,c,e
7,5	75	9,38	b,d,f	a,c,e
8,0	80	10,0	b,d,f	a,c,e

*Refer to Table 6.1 and to Figure 6.9

TABLE 6.2

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7.0 INTRODUCTION

In Chapter 6 it was shown that rapid mixing is the stage in the overall coagulation-flocculation process where destabilization reactions occur and where primary, pin-point flocs commence growth. A necessary adjunct to destabilization is the inducement of primary particles to approach close enough together, make contact and progressively form larger agglomerates. This stage in the overall process is termed flocculation.

There are two stages in the flocculation process: The first, given the name *perikinetic* flocculation, arises from thermal agitation (Brownian movement) and is a naturally random process. Flocculation during this stage commences immediately after destabilization and is complete within seconds since there is a limiting floc size beyond which Brownian motion has no or little effect.

Furthermore, although the potential energy barrier existing between colloidal particles may be overcome by the thermal kinetic energy of Brownian movement (see Section 2.7.1), as the particles progressively coalesce the magnitude of the energy barrier increases approximately proportional to the area of the floc, so that eventually perikinetic flocculation of such potentially repellant particles must cease(39).

The rate of flocculation or the rate of decrease in the number of particles of a suspension due to perikinetic flocculation may be described by a second order rate law. For example, in a turbid water containing 10^6 particles per ml, the particle number concentration would be reduced by half within a period of about 6 days; provided all the particles were completely destabilized and the particles did not become too large and be outside the range of Brownian movement. The theoretical development of perikinetic flocculation is dealt with in Section 7.1.

The second stage in the flocculation process is given the name *orthokinetic* flocculation and arises from induced velocity gradients in the liquid. Such velocity gradients may be induced by setting the liquid in motion by (a) passage around baffles or mechanical agitation within a flocculation reactor; (b) the tortuous path through interstices of a granular filter bed; (c) where flocs are sufficiently formed, by sedimentation within a settling basin and so on. The effect of velocity gradients within a body of liquid is to set up relative velocities between particles thereby providing opportunity for contact.

For a given flocculating system, the principal parameter governing the rate of orthokinetic flocculation is the velocity gradient applied. The degree or extent of flocculation is governed by both applied velocity gradients and time of flocculation. These two parameters influence the rate and extent of particle aggregation and the rate and extent of breakup of these aggregates.

The theoretical development and practical applications of the orthokinetic flocculation phenomenon are dealt with in Section 7.2.

Figure 7.1 shows that there are several variations in the layout of the overall coagulation-flocculation process (12): (a) destabilization (rapid mix) flocculation-sedimentation-filtration; (b) as for (a) but with the inclusion of a coagulant-control filter, addition of flocculant aid to the filter influent and dual or mixed-media filters; (c) direct filtration utilising a flocculation basin with either a cationic polyelectrolyte added before rapid mixing (as shown) or alternatively, alum added before rapid mixing and flocculant aid before filtration; (d) direct filtration with a contact basin between the rapid mix stage and filtration. (The objective of the basin is not to provide flocculation or settling but rather a lag time to provide opportunity for response to the control filter); (e) direct filtration with only rapid mixing before filtration.

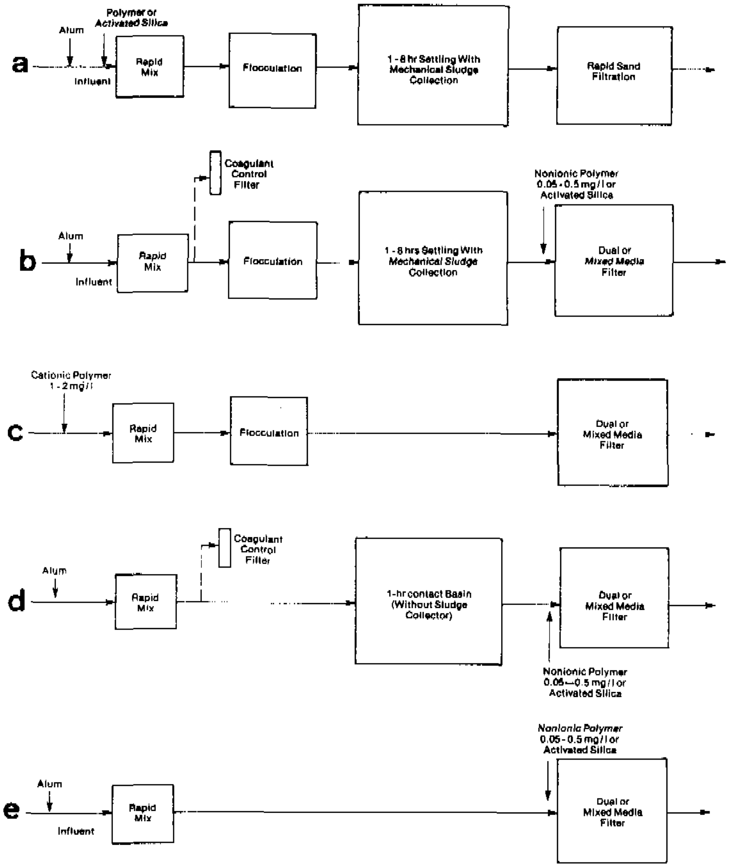


FIGURE 7.1: (a) Flow Sheet for Typical Conventional Plant; (b) As for (a) But With a Coagulant Control Filter; (c) Direct Filtration With Flocculation; (d) Direct Filtration With Contact Basin; (e) Direct Filtration With Rapid Mixing Only. (From Culp(12), With Permission of the American Water Works Association).

Alternatives (a) to (c) above require the inclusion of a flocculation reactor or basin whereas alternatives (d) and (e) rely on velocity gradients produced within a filter bed. Induced velocity gradients within flocculation basins is dealt with in section 7.3. Application of velocity gradients through the granular media of filter beds is given the name *contact flocculation* and is dealt with in Section 7.4.

7.1 PERIKINETIC FLOCCULATION

Von Smoluchowski (37, 38) developed a model for perikinetic flocculation where the frequency of collisions was obtained from the diffusional flux of particles towards a single stationary particle. He assumed that particles diffused towards the stationary particle in a radial direction. The number of particles diffusing radially inwards through the surface of a sphere centred on the stationary particle is proportional to the Brownian diffusion coefficient of the particles, the surface area of the sphere and the particle concentration gradient in the radial direction. Since the diffusion is assumed to be radial the number of particles diffusing radially inwards is equal to the number of collisions with the central particle. Assuming that the central particle also experiences diffusion, von Smoluchowski's equation for perikinetic flocculation is:

$$I_{ij} = 4\pi D_{ij} R_{ij} n_i n_j \qquad (7.1)$$

where I_{ij} = the number of contacts per unit time between particles of radius R_i and R_j

D_{ij} = the mutual diffusion coefficient of particles i and j (approximately $D_i + D_j$)

R_{ij} = radius of interaction of the two particles, i.e. the distance between centres of two particles forming a lasting contact, i.e.

$$R_{ij} = R_i + R_j$$

n_i, n_j = respective number concentration of i and j particles.

If velocity gradients exist in the body of liquid of a magnitude dv/dz greater than approximately 5 s^{-1} and if particle sizes are larger than 1 micrometer the effect of perikinesis is negligible and orthokinetic flocculation need only be considered under such conditions.

7.2 ORTHOKINETIC FLOCCULATION

7.2.1 Theoretical Development

Once perikinetic flocculation is complete the only way in which appreciable contact between particles can be promoted is to induce shear motion in the liquid. This is achieved by inducing velocity gradients whereby particles achieve mutual contact by movement with the surrounding liquid. The process of floc aggregation by this procedure is termed orthokinetic flocculation.

The greater the velocity gradients induced in the liquid the more particle contacts there will be within a given time. However, the greater the velocity gradients the smaller will be the ultimate floc size due to a continuous breakdown of the larger flocs. Hence, for a given velocity gradient there will be a limiting flocculation time beyond which floc particles will not grow further. The lower the velocity gradient the longer will be the time needed to reach the optimum floc size, but the larger will be the final floc size.

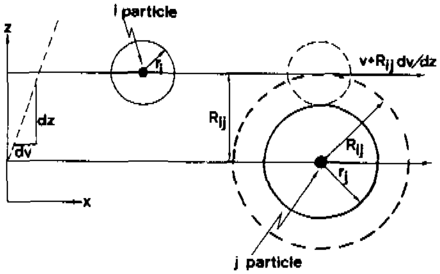


FIGURE 7.2: Contact Between Two Particles, i and j, Moving Under the Influence of a Velocity Gradient, dv/dz.

Von Smoluchowski(37, 38) formulated a mathematical model for the orthokinetic flocculation of colloidal particles under laminar flow conditions.

Two particles, i and j, are suspended in a liquid moving in the x direction in laminar flow. The velocity of the j particle is v and the velocity gradient in the z direction is $\frac{dv}{dz}$, the centre of the j particle is the origin of a set of Cartesian coordinates (See Figure 7.2).

For the i particle to come into contact with the j particle it must be brought close enough for London-van der Waal forces of attraction to 'pull' and hold the two particles together. The locus of the i particle or any number of i particles satisfying this requirement is a sphere centred at the origin of the coordinate system and with a radius $R_{ij} = (r_i + r_j)$. The sum of the radii of the spheres R_{ij} defines the range of influence of London-van der Waal forces for the individual i and j particles. The larger the particles, the narrower, *in a relative sense,* is the zone of influence of London-van der Waal forces beyond the surface of the particle; the closer therefore is the diameter of the particle to the 'effective' diameter (See Figure 7.3).

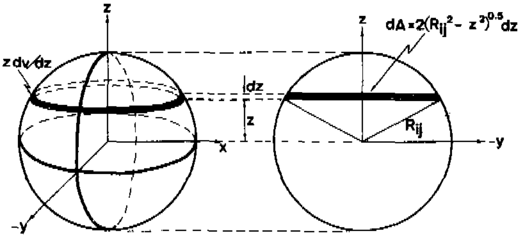


FIGURE 7.3: Zone of Influence Around Central j particle.

If the particles follow the stream lines that would develop in their absence, the number of i particles making contact with the j particles would equal the product of the rate of flow q into the sphere, and the number of i particles per unit volume of fluid.

The velocity of flow at distance z from the j particle = $z\frac{dv}{dz}$ (relative to the j particle).

The area through which this flow takes place = $dA = 2\sqrt{R_{ij}^2 - z^2}dz$. Hence the rate of flow into the area dA is given by:

$$dq = z\frac{dv}{dz}\{2\sqrt{R_{ij}^2 - z^2}dz\} \tag{7.2}$$

If the number of i particles per unit volume is n_i, the number of 'contacts' H_i of i particles with the central j particle in unit time is:

$$H_i = 2\int_{z=0}^{z=R_{ij}} n_i dq = 2n_i \int_{z=0}^{z=R_{ij}} z\frac{dv}{dz}\ 2\sqrt{R_{ij}^2 - z^2}dz \tag{7.3}$$

For a constant velocity gradient over the range of integration:

$$H_i = 4n_i\left(\frac{dv}{dz}\right)\int_0^{R_{ij}} z\sqrt{R_{ij}^2 - z^2}dz = 4n_i\frac{dv}{dz}\left\{\frac{R_{ij}^3}{3}\right\} = \frac{4}{3}n_i\left(\frac{dv}{dz}\right)R_{ij}^3 \tag{7.4}$$

For n_j central j particles, the number of contacts between all i particles and j particles per unit time is given by:

$$H_{ij} = \frac{4}{3}n_i n_j R_{ij}^3 \frac{dv}{dz} \tag{7.5}$$

where $\frac{dv}{dz}$ = velocity gradient in laminar flow.

The application of von Smoluchowski's orthokinetic flocculation equation to the design of flocculation tanks is limited in that his theoretical treatment is based on laminar flow conditions. The more usual condition existing for the practicable velocity gradients applied during flocculation is a turbulent regime(11).

Since the local velocity gradients are not known in turbulent mixing, Camp and Stein(7) replaced the velocity gradient term dv/dz by a measurable average value termed the root mean square velocity gradient, G, which is defined by Camp(8) as follows:

$$G = (W/\mu)^{1/2} \qquad (7.6)$$

where μ = absolute viscosity and

W = *dissipation function* = total power dissipated divided by the volume of chamber or conduit etc. = mean value of the work of shear per unit volume per unit time.

Replacing dv/dz in Equation 7.5 by G, Camp and Stein's equation for orthokinetic flocculation is given by:

$$H_{ij} = \frac{4}{3} n_i n_j R_{ij}^3 G \qquad (7.7)$$

The principal objection to the use of the average velocity gradient, G, is that it does not describe the length scale over which local velocity gradients extend. That is, velocity gradients which extend for a given mixing length do not influence the flocculation of particles which are larger than this distance.

Fair and Gemmell(13) extended Von Smoluchowski's Equation (7.5) to describe the rate of change in number concentration of flocs of a given size R_k:

$$\frac{dn_k}{dt} = \frac{2}{3}\left[\sum_{\substack{i=1\\ j=k-1}}^{k-1} n_i n_j R_{ij}^3 - 2n_k \sum_{i=1}^{\infty} n_i R_{ik}^3\right]\frac{dv}{dz} \qquad (7.8)$$

The first term in the brackets describes the formation of particles of radius R_k from a range of particles, i.e. from primary particles (i and j = 1) to (k - 1) fold particles. For example, the joining of a (k - 1) fold particle and a primary particle produces a k - fold particle with radius R_k. The second term in the brackets depicts the elimination of k - fold particles due to their collisions with all other particles, i.e. with the full range of particles from i = 1 (primary particles) to infinity.

In all the equations above floc breakup was not considered. Furthermore, all collisions were assumed to result in lasting contact.

Harris and Kaufman(15) and Harris, Kaufman and Krone(16) modified Equation 7.8 to include floc breakup and the possibility of non-lasting collisions. They considered the case of k = 1, which describes the rate at which primary (1 - fold) particles are removed from the system. Their expression for the rate of change in primary particle concentration is as follows:

$$\frac{dn_1}{dt} = - \frac{\alpha a^3}{\pi} \delta \phi \; n_i \frac{dv}{dz} \qquad (7.9)$$

where α = fraction of collisions which result in aggregation

a = ratio of collision radius of a floc to its physical radius

ϕ = floc volume fraction

δ = size distribution function given by

$$\delta = \frac{\sum_{i=0}^{p-1} n_i (i^{1/3} + 1)^3}{\sum_{i=0}^{p} i \; n_i}$$

The maximum floc size permitted is p-fold. Harris _et al_ presented other distribution functions for various floc formation and breakup models. Hudson(17) adopted a different approach by assuming that in a continuous flow system a simplified bimodal floc size distribution is valid. In a system composed of only primary particles and large flocs, assuming size variations within each group are small compared to the difference between the groups, the removal of primary particles is hypothesised to occur primarily by their collisions with flocs. Accordingly Equation 7.8 is simplified to:

$$\frac{dn_1}{dt} = - \frac{4}{3} n_1 n_F \; R_F^3 \frac{dv}{dz} \qquad (7.10)$$

where

R_F = radius of flocs

n_F = floc number concentration

Flocculation as described by the above equations probably occurs whenever applied velocity gradients are linear over a distance of a particle diameter. In a turbulent regime, however, flocculation kinetics are better described by turbulent diffusion.

Argaman and Kaufman(2, 3) proposed a diffusion model for orthokinetic flocculation analogous to that of von Smoluchowski for perikinetic flocculation. It is based on the hypothesis that particles suspended in a turbulent regime experience a random motion resembling gas molecules. In their analysis a simplified bimodal floc size distribution comprising primary particles and large flocs was assumed. This assumption was also made by Hudson(17). Argaman and Kaufman experimentally verified the validity of the bimodal distribution by analysing floc size measurements. Their expression for the rate of collision of primary particles and flocs is given by:

$$H_{1F} = 4\pi \, K_S R_F^3 n_1 n_F \, \overline{u^2} \tag{7.11}$$

where

K_S = proportionality coefficient expressing the effect of the turbulence energy spectrum on the effective diffusion coefficient.

R_F = radius of floc

n_1, n_F = number concentration of primary particles and flocs respectively

$\overline{u^2}$ = mean square velocity fluctuation, which is related to the root mean square velocity gradient, G, and is a measure of the intensity of turbulence.

Although Equation 7.11 was derived for orthokinetic flocculation using the concept of turbulent diffusion, it is equivalent in form to the orthokinetic flocculation equation of von Smoluchowski using the concept of laminar flow velocity gradients. In fact all the equations derived for particle aggregation kinetics during orthokinetic flocculation are similar in form to Equation 7.5. The differences lie in the constant terms and the definitions of velocity gradient.

It was recognised by Argaman and Kaufman that two opposing processes are responsible for the change in particle concentration during flocculation, that is, aggregation of primary particles and small flocs to form larger flocs (as described by Equation 7.11) and the breakup of flocs into smaller fragments. The breakup mechanism assumed by Argaman and Kaufman is described by the rate of formation of primary particles by shearing from the floc surface, i.e.

$$\left.\frac{dn_1}{dt}\right|_{\text{breakup}} = B\,R_F^2\,\frac{n_F}{R_1^2}\,\overline{u^2} \qquad (7.12)$$

where

B = breakup constant

Parker, Kaufman and Jenkins(28, 29) on reviewing alternative mechanisms for floc breakup (i.e. erosion of primary particles from the floc surface or floc deformation and subsequent splitting) concluded that the surface erosion concept used by Argaman and Kaufman was the more plausible (although, as will be seen in Section 7.2.5.1 there still remains a certain inadequacy in the assumed breakup equation). The rate of change in concentration of primary particles is thus given by combining Equations 7.11 and 7.12, i.e.

$$\frac{dn_1}{dt} = -4\pi\alpha K_S R_F^3 n_1 n_F \overline{u^2} + B\frac{R_F^2}{R_1^2}\,n_F\overline{u^2} \qquad (7.13)$$

where

α = *fraction of particle collisions resulting in* lasting aggregation

Argaman and Kaufman applied Equation 7.13 to the case of a single, completely mixed continuous flow tank reactor and, at steady state, obtained the following equation:

$$(n_0 - n_1) = (4\pi\alpha K_S R_F^3 n_1 n_F \overline{u^2} - B \frac{R_F^2}{R_1^2} n_F \overline{u^2})T \qquad (7.14)$$

Rearranging Equation 7.14:

$$\frac{n_0}{n_1} = \frac{1+4\pi\alpha K_S R_F^3 n_F \overline{u^2} T}{1+\dfrac{B\ R_F^2 n_F \overline{u^2} T}{n_0 R_1^2}} \qquad (7.15)$$

where

n_0 = number concentration of primary particles at time T = 0

n_1 = number concentration of primary particles at time T

n_0/n_1 = is referred to as the performance parameter.

7.2.2 Working Equation

In order to develop a working equation incorporating experimentally measurable parameters, Argaman and Kaufman made a number of assumptions as follows:

1. The average floc size is closely related to the mean square fluctuating velocity as follows:

   $$R_F = K_2/\overline{u^2} \qquad (7.16)$$

   where

   K_2 is a constant

   They showed experimentally that, for practical purposes, this assumption is valid.

2. The mean square fluctuating velocity fluctuations can be estimated from the root mean square velocity gradient as follows:

   $$\overline{u^2} = K_p G \qquad (7.17)$$

where

K_p = performance parameter dependent on the type of stirring arrangement and referred to as 'stirrer performance coefficient'

This assumption was supported by experimental observations using a hot-film anemometer for a range of G values from 30 to 240 sec^{-1}. For a stake and stator stirrer arrangement they found $K_p = 0{,}0458\ cm^2\ sec^{-1}$ and for a turbine stirrer $K_p = 0{,}0233\ cm^2\ sec^{-1}$.

The difference in K_p for the different stirrers supports the contention that G is a parameter whose influence is dependent on one particular stirrer arrangement and reactor configuration.

3. Assuming spherical particles, the total volume of flocs in a reactor is given by:

$$\phi = \frac{4}{3}\pi n_F R_F^3 \qquad (7.18)$$

where

ϕ = floc volume fraction.

4. The aggregation - collision ratio, α, is constant. They point out, however, that as the time of flocculation increases the flocs become more compact and of a more regular shape, and therefore the probability of successful adhesion on collision decreases.

Substituting Equations 7.16, 7.17, and 7.18 into Equation 7.15 and describing a flocculation constant, K_F, as:

$$K_F = 3\alpha\phi \qquad (7.19)$$

and a breakup constant, K_B, as:

$$K_B = \frac{3}{4\pi} \; \frac{B\phi K_p^2}{n_0 R_1^2 K_2} \qquad (7.20)$$

the flocculation equation becomes:

$$\frac{n_0}{n_1} = \frac{1+K_A GT}{1+ K_B G^2 T} \qquad (7.21)$$

where

$$K_A = K_F K_S K_P$$

K_B and K_A are constants for a single tank.

7.2.3 Flocculation Reactors in Series

By making a further assumption that with a number of reactors, m, in series the constants K_A and K_B retain the same values, a general working equation for the i-th tank in the series is given by:

$$\frac{n_{i-1}}{n_i} = \frac{1+ K_A GT/m}{1+ K_B \frac{n_0}{n_{i-1}} G^2 T/m} \qquad (7.22)$$

The overall performance of an m tank series system is therefore given by:

$$\frac{n_0}{n_m} = \frac{(1+ K_A GT/m)^m}{1+ K_B G^2 T/m \sum_{i=0}^{m-1} (1+ K_A GT/m)^i} \qquad (7.23)$$

By carrying out experiments using a synthetic turbid water with the number of reactors progressively increasing from one to four, Argaman and Kaufman demonstrated the validity of Eq. 7.23. To illustrate tne inter-relationship between the various parameters, Figure 7.4(4) shows the rms velocity gradient, G, plotted against total retention time, T, for a series of reactors m (= 1 to 4) and for various values of performance parameter n_0/n_m. The marked beneficial effect of compartmentalization is evident, especially where higher performances are desired. For example, if 75% removal of primary particles ($n_0/n_m = 4$) is desired, a single reactor would require a retention time of 2000 s whereas four reactors in series would require 800 s, that is, less than half the retention time.

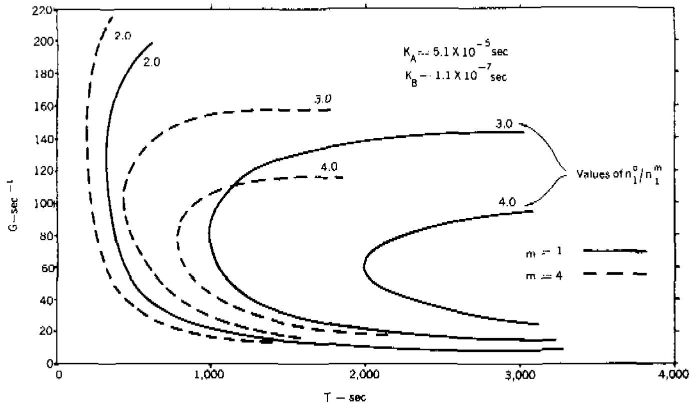


FIGURE 7.4: Performance of Flocculation System As Related to G, T and m. (From Argaman$^{(4)}$, With Permission of the American Water Works Association).

7.2.4 Product GT as Design Parameter

Of particular note in Figure 7.4 is the fact that the product GT, commonly used as a design parameter (see for example, Camp$^{(9)}$) does not adequately identify the conditions for a given flocculation performance. For example, from Figure 7.4 at a desired performance $n_0/n_m = 3$ using four reactors in series, there is a minimum retention time of 2000 s below which that particular performance cannot be achieved. regardless of the magnitude of G. The inadequacy of the GT product as a design parameter is because the phenomenon of floc breakup is not accomodated. An exception is where G values are low or, alternatively, K_B is low (very strong flocs) and Equation 7.23 approaches $n_0/n_m = (1+ K_A GT/m)^m$. In this case, performance for a particular flocculation system is directly dependent on the product GT.

7.2.5 Experimental Determination of Flocculation Parameters

The equations describing both the aggregation and breakup phases of the flocculation process have been set out in the preceeding sections. These equations contain certain "constants" which must be evaluated for each particular water. One method is to carry out continuous type pilot plant trials. However, this has the disadvantage that relatively complicated and costly apparatus and lengthy testing procedures are required. A further possibility is the use of batch testing procedures. However, many workers consider it essential that the experimental determination of flocculation parameters be carried out using pilot plant studies (for example, Argaman$^{(4)}$). Furthermore, it has been stated that the application of batch test data is appropriate for plug flow reactors only (O'Melia $^{(26)}$). Regardless of this, if it were shown possible to determine the appropriate parameters of flocculation by a simple batch testing procedure, a powerful means would be available to design engineers for the design of continuous completely mixed flocculation systems. Without the incentive of a quick and inexpensive experimental procedure and apparatus, designers through economic necessity (especially for relatively small plants) would tend to base design on subjective assessments, a practice not unusual at present.

Bratby et al$^{(5, 6)}$, by correlating batch test data with those from continuous type tests, demonstrated the theoretical link between batch or plug flow behaviour and continuous test performance. They showed that, by taking cognisance of the appropriate (different) formulations, batch test data can be used for the design of in-series completely mixed flocculation reactors. Their basic premise was that, in Equation 7.23, if K_A and K_B remain constant for all tanks in a series of completely mixed reactors then these constants should theoretically remain unchanged when the number of tanks is increased to infinity, that is, for plug flow or batch conditions.

Batch test results are governed by a relationship of the form given by Equation 7.13. Substituting Equations 7.16, 7.17 and 7.18 into Equation 7.13 and expressing $K_A = K_F K_S K_P$ and $K_B = \frac{3}{4\pi}(B\phi K_p^2)/(n_0 R_1^2 K_2)$ as before, the equivalent flocculation equation for a batch system is given by$^{(5, 6)}$:

$$\frac{dn_1}{dt} = -K_A n_1 G + K_B n_0 G^2 \tag{7.24}$$

Integration of Equation 7.24 yields

$$n_1 = \frac{K_B}{K_A} n_0 G + n_0 \left(1 - \frac{K_B}{K_A} G\right) e^{-K_A G T}$$

Rearranging

$$\frac{n_0}{n_1} = \left[\frac{K_B}{K_A} G + \left(1 - \frac{K_B}{K_A} G\right) e^{-K_A G T} \right]^{-1} \tag{7.25}$$

The experimental apparatus and procedures recommended by Bratby et al for determining the "constants" K_A and K_B by a batch test procedure are described in detail in Section 8.4.

7.2.5.1 Inconstancy of K_B

Although K_A and K_B have both been described above as constants, this is strictly only valid for K_A. Due to an inadequacy of the assumed break-up mechanism in the above analyses, K_B may assume a constant value for only one particular G value. However, this does not deter from the value of the relationships describing flocculation performance since the same variation in K_B is evident in both batch and continuous performance (see Section 8.4.4). For convenience, therefore, when analysing data from batch tests, the value of K_B may be empirically related to G by an expression of the form

$$G = \exp \left(\frac{K_B - k_2}{k_1}\right) \tag{7.26}$$

where, from section 8.4.4, k_1 and k_2 are constants for a particular water.

Re-analysing the data of Bratby et al(5) for a synthetic (kaolin clay) turbid water using alum as coagulant, K_B is related to G as follows:

$$G = \exp\left(\frac{7{,}72.10^{-7} - K_B}{0{,}87.10^{-7}}\right)\ s^{-1}$$

For a humic coloured water with zero turbidity and using alum as coagulant(6):

$$G = \exp\left(\frac{15{,}2.10^{-6} - K_B}{3{,}04.10^{-6}}\right)\ s^{-1}$$

(See Figures 8.8a and 8.8b respectively, Section 8.4.4).

For the turbid suspension $K_A = 2{,}5.10^{-4}$ and for the coloured water $K_A = 3{,}09.10^{-4}$, both values remaining constant under the full range of conditions tested(5, 6).

7.2.5.2 Scale-Up Effects

A factor of crucial importance is the applicability of bench scale results to the design of full scale units, that is, whether such results can be applied directly or whether scaling-up factors are required. Argaman and Kaufman(2, 3) and Argaman(4) found good correlation between results obtained from laboratory scale continuous type experiments and those obtained from a full scale plant treating the same type of water. They concluded that laboratory scale continuous experiments may be successfully extrapolated to full scale design. The good correlation between batch test results and continuous experiments demonstrated by Bratby et al(5, 6) indicates that batch data may also be directly applied to full scale design provided the geometry and stirring mechanisms of the laboratory and full scale reactors are similar.

7.3 DESIGN OF FLOCCULATION BASINS

7.3.1 General

For a given destabilized water and flocculation device, the principal parameters governing the effective degree of flocculation are the retention time and velocity gradients applied. These parameters influence the rate and extent of particle aggregation and the rate and extent of break-up of these aggregates. The kinetics of the flocculation process are dependent not only on the type of raw water, but also on the mode of destabilization, that is, on the type of primary coagulant used, e.g. aluminium sulphate, ferric chloride, some form of polyelectrolyte, etc., and any flocculant aid added. Before design of a flocculation system, therefore, a thorough testing program must be undertaken. The first stage is to identify the most appropriate chemical(s) to achieve the required degree of clarification (See Sections 8.1 and 8.2). At the end of this stage one will presumably have a number of alternatives. The second stage is to assess the alternatives in terms of the efficiency of flocculation (See Section 8.4).

Having assessed each chemical combination alternative in terms of both destabilization (clarification) efficiency and flocculation efficiency, some form of final choice in terms of overall economics is required. An overall assessment of capital and capitalised running costs for each alternative is carried out which includes chemical (running) costs and the cost of the flocculation system.

7.3.2 Types of Flocculation Device

There are several methods by which velocity gradients may be induced in a body of liquid. These include: 1) baffled chambers; 2) diffused air; 3) spiral flow; 4) reciprocating blades and 5) rotating blades. Each of these methods is described below.

7.3.2.1 Baffled Chambers

Baffled flocculation chambers, probably among the earliest types of flocculation basins, may be installed either with over and under baffles (an example of which is shown in Fig. 7.5) or around the end baffles. The latter configuration may in some cases be preferable since it is easier to drain and clean(18). Advantages of baffled chambers are that they are virtually maintenance free and short circuiting is minimised(22). A serious disadvantage, however, is that since most of the head loss occurs at the

180° bends, velocity gradients are probably excessive at the bends and too low along the straight sections(9). Furthermore, with such devices, velocity gradients are wholly dependent on the flow rate through the basin and, therefore, offer no degree of control.

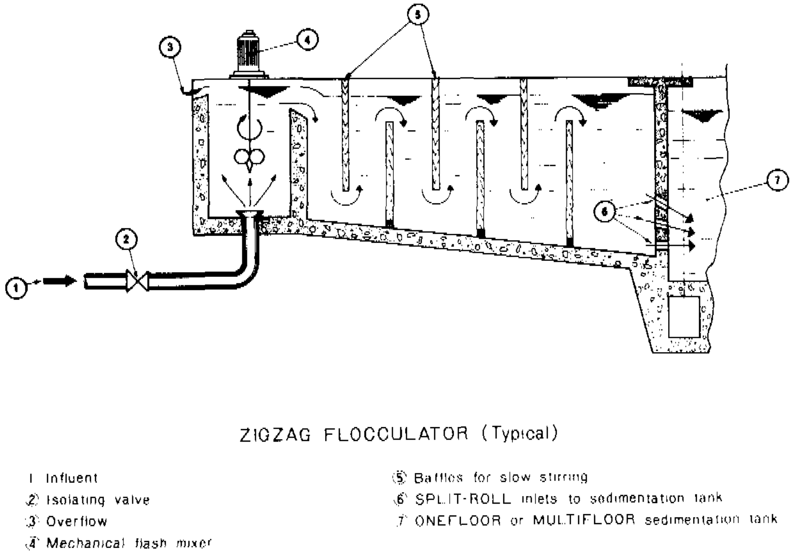


FIGURE 7.5: Baffled Flocculation Chamber (Zig-Zag, Courtesy Compagnie Européenne de Traitement des Eaux).

For baffled flocculation basins, the average velocity gradient, G, is computed from Equation 7.6 i.e.:

$$G = (W/\mu)^{1/2}$$

where μ = absolute viscosity of liquid and W, the dissipation function, is given by(9):

$$W = \gamma h_L/T \tag{7.27}$$

where γ = weight/unit volume of liquid (N m^{-3})

h_L = head loss (m)

T = retention period (s)

7.3.2.2 *Diffused Air*

Flocculation in a body of liquid may be achieved by introducing air through diffusers at the bottom. The velocity gradient produced in this case may be controlled to a certain extent by regulating the air flow.

From Camp(9), the expression for the flow rate of free air, Q_a, required for a mean velocity gradient G, converted to metric units, is given by

$$Q_a = G^2 \mu V(H/2 + 10{,}33)/(H.10^5) \qquad (7.28)$$

Where μ = absolute viscosity = 10^{-3} N s m^{-2} for water at 20°C;

V = volume of liquid in basin (m^3);

and H = depth of diffusers (m).

A disadvantage of diffused air flocculators is that with practicable bubble sizes produced by available diffusers, the local velocity gradient produced at the bubble surface is much higher than the mean existing (and desired) for the whole volume. This maximum local velocity gradient G_{max} is given by(9).

$$G_{max} = g(\rho - \rho_1)\, D_b/6\mu \qquad (7.29)$$

where ρ_1 = density of air in bubble (kg m^{-3});

ρ = density of liquid (kg m^{-3});

and D_b = diameter of bubble (m)

Table 7.1 shows values of G_{max} for a range of bubble sizes (water at 20°C).

TABLE 7.1: Values of Velocity Gradients Produced by a Range of Bubble Sizes

Bubble Diameter (mm)	G_{max} (s^{-1})
0,01	16
0,05	82
0,1	163
0,15	245
0,5	816
1,0	1633
2,0	±3265

It is seen that in most cases bubble sizes must be extremely small (± 10 micrometers in, say, the final compartment of an in-series flocculation system). Although the production of such bubbles is practicably feasible (for example by a dissolved-air precipitation technique) inevitably flotation of suspended flocs would occur which, even if a float removal mechanism were provided at the top of the flocculation unit, would progressively impair the rate of flocculation by reducing the number of flocculating particles.

7.3.2.3 Spiral Flow

Velocity gradients may be induced by introducing liquid into a basin tangentially at high velocity. The mean velocity gradient, G, for the basin (which may be circular or square) is computed using Equations 7.6 and 7.27, taking h_L as the velocity head at the inlet. Disadvantages with this method are that velocity gradients are not uniformly distributed and passage from one basin to the next in series may result in excessive floc breakup(9).

7.3.2.4 Rotating Blades

Examples of rotating blade type flocculation devices are shown in Fig. 7.6. Generally, such devices are of two types: horizontal shaft (Fig. 7.6a) and vertical shaft (Fig. 7.6b). Horizontal shaft units have under-water bearings which require maintenance. In some cases the drive shaft passes through to a dry well, which often gives rise to problems of leakage, or the drive may be from overhead via V-belts or chains. In this case V-belts

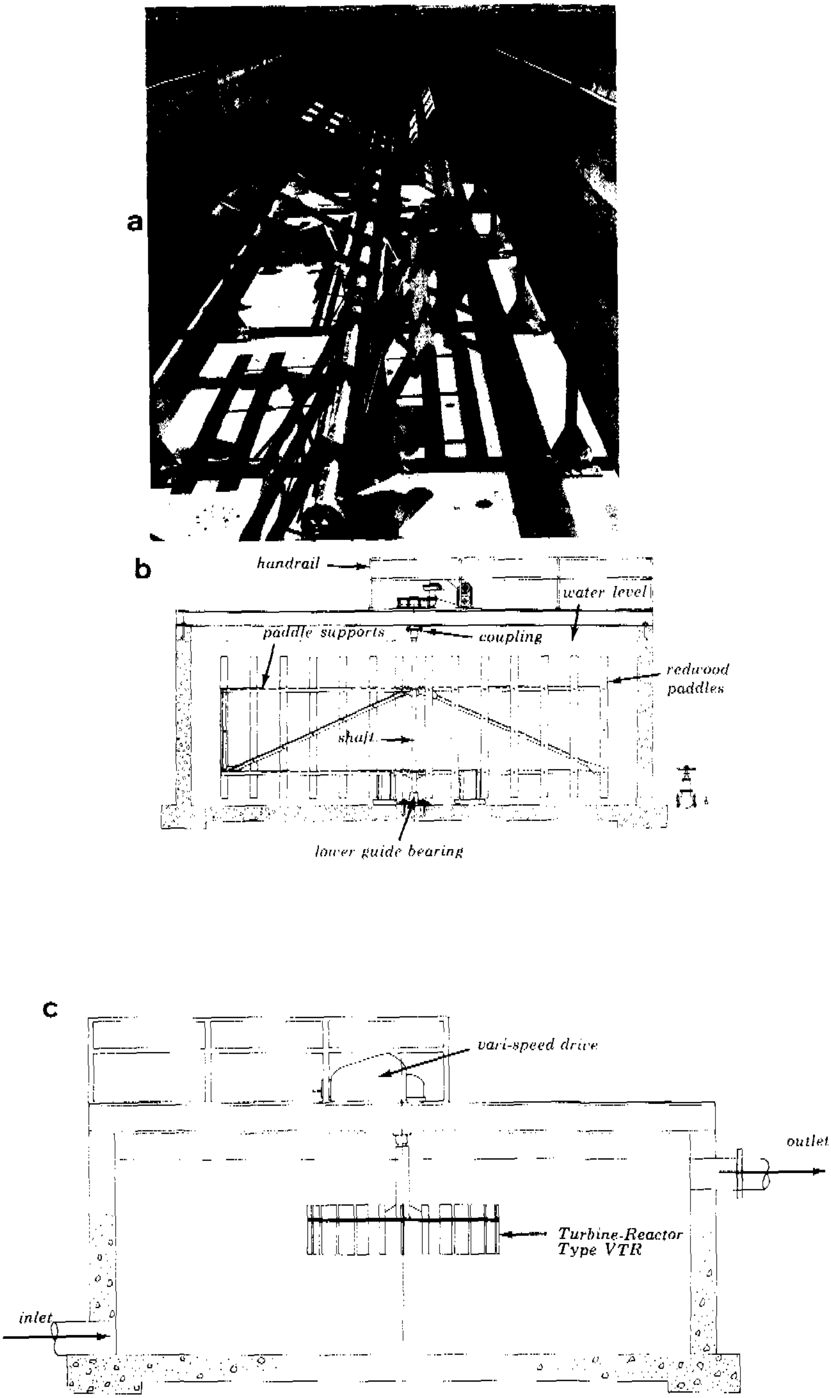


FIGURE 7.6: Examples of Rotating Blade Flocculators. (Courtesy Eimco).

are often preferred since they are usually trouble free, unlike chains which may require frequent replacement.

An advantage of horizontal shaft units is that compartmentalization is simple. With adjacent sections along the drive shaft carrying different configurations of agitators different G values are produced for one particular drive shaft rotational speed. With vertical shaft flocculators, each drive unit usually serves only one compartment.

With most designs of horizontal shaft flocculators, the provision of stators within the flocculation basin to minimise rotation of the water with the blades is difficult. It would appear desirable, therefore, to arrange paddles perpendicularly to the shaft, rather than parallel.

The principal advantages of vertical shaft rotary devices are that underwater bearings are not required; the drive unit is above the water level and the arrangement for stators is simple. A further advantage is that with combined flocculation-sedimentation units (see Section 7.3.5) vertical shaft flocculators are simpler to install than horizontal shaft units.

A further rotating flocculation device is the turbine flocculator, an example of which is shown in Figure 7.6c. A disadvantage of such units is that there is a much wider diversity of G values within the flocculation basin for a given mean velocity gradient - being high in the vicinity of the device and low near the walls of the basin. The different (lower) flocculation performance achieved by such devices compared to those accomodating as much of the flocculation basin volume as possible has been pointed out by Argaman and Kaufman(2, 3)

When velocity gradients are induced by mechanical mixing, the value of the dissipation function, W, may be estimated from the drag force of the stirring blades and the distance moved per second. The drag force for any body in motion in a liquid is given by:

$$F_D = C_D . A\gamma\frac{v^2}{2g} \qquad (7.30)$$

where

C_D = drag coefficient

A = cross-sectional area of the submerged object in a plane perpendicular to the direction of the motion (m^2).

V = relative velocity of the object with respect to the liquid ($m\ s^{-1}$)

γ = weight/unit volume of liquid ($N\ m^{-3}$).

In order to simplify design of vertical paddle type devices it is desirable that rotor paddles be mounted parallel to the shaft on arms attached to the shaft. The velocity of a paddle with respect to the tank is then proportional to its distance from the shaft.

A flocculation tank must have several rotor paddles at varying distances from the shaft. The area between the paddles should comprise stators fixed to the tank to minimise rolling of the water.

The value of dissipation function W for all the paddles in a tank is given by(9):

$$W = \Sigma\frac{F_d v}{V} = \Sigma\frac{C_D A\gamma v^3}{2gV} = \frac{1{,}24.10^5 C_D (1-k)^3 S_s^3}{V}\Sigma A {r_b}^3 \qquad (7.31)$$

C_D = drag coefficient = 2,0 for flat blades for rotating devices(9)

S_s = speed of rotation of shaft ($rev\ s^{-1}$)

kS_s = speed of rotation of water ($rev\ s^{-1}$)

V = volume of water in tank (m^3)

A = cross-sectional area of each blade in the plane perpendicular to direction of motion (m^2)

r_b = distance of centre of each blade from shaft (m)

The root mean square velocity gradient is given by:

$$G = \sqrt{\frac{W}{\mu}} = \sqrt{\frac{1,24.10^5.C_D.(1-k)^3 S_s^3}{V \mu} \Sigma A r_b^3} \quad s^{-1} \qquad (7.32)$$

where

μ = absolute viscosity of liquid ($=10^{-3}$ N s m^{-2} for water at 20°C).

The speed of rotation of the water ($k S_s$) is difficult to pre-determine since rotary stirring devices set the liquid in spiral motion with an average angular velocity less than the velocity of the rotors and with the velocity beyond the central core diminishing with distance from the centre. In a few plants, the width of the paddles is so great that the water is carried along at approximately that of the paddles(9). The only mixing in such cases arises from velocity gradients set up between the outside edges of the paddles and the walls of the tank.

As a guide, k usually falls within the range 0,2 at high impeller speeds (0,03 to 0,09 rev s^{-1}) to 0,35 at low impeller speeds (0,015 to 0,05 rev s^{-1}) when $\Sigma A r_b^3$ for stators is equal to $\Sigma A r_b^3$ for rotors(9). Bratby et al(5, 6) found k had a constant value of 0,24 for the full range of rotational speeds used in their experiments.

7.3.2.5 *Reciprocating Blades*

Figure 7.7 illustrates two types of reciprocating blade flocculation devices. Determination of velocity gradients produced by such devices is carried out using the principle of simple harmonic motion. The relative velocity of blade and liquid changes continuously throughout a cycle. To obtain values for the mean velocity gradient, G,

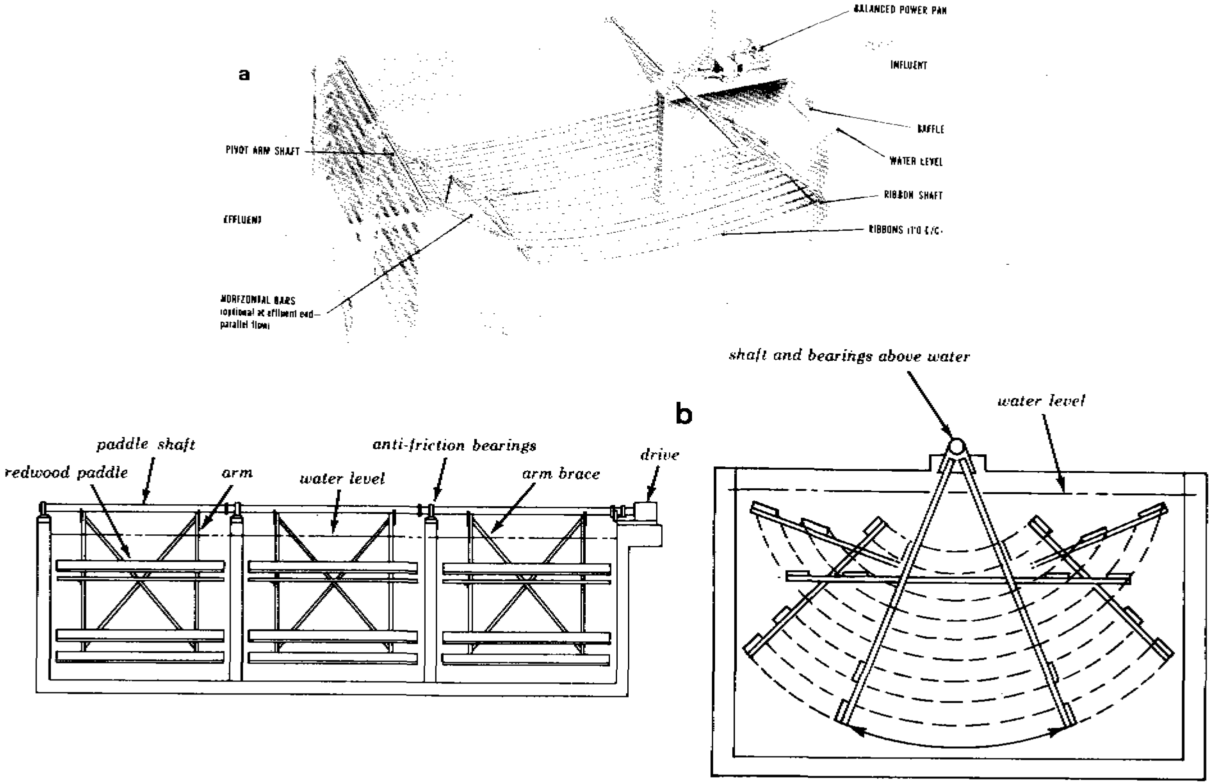


FIGURE 7.7: Examples of Reciprocating Blade Flocculators: (a) Courtesy Dorr-Oliver; (b) Courtesy Eimco

it is necessary to compute the mean value of the dissipation function, W, throughout a cycle. Camp(9) presents an expression for G which, in terms of metric units, is as follows:

As before, $G = (W/\mu)^{1/2}$ (7.6)

$$\text{where } W = \frac{6{,}58.10^3 . C_D D^3 S_s^3}{V} \Sigma A \qquad (7.33)$$

and C_D = drag coefficient = 3,0 for flat blades for reciprocating devices(9);

D = length of stroke of paddles in reciprocating motion (m);

S_s = speed of rotation of drive shaft (rev s^{-1}), or number of complete strokes per unit time (s^{-1})

V = volume of liquid in flocculation basin (m^3);

ΣA = total cross sectional area of blades in plane perpendicular to direction of motion (m^2).

7.3.2.6 Start-Up of Flocculation Devices

At start-up of a flocculation device, particularly those using rotating blades, the liquid is stationary and the value of k in Equation 7.31 is zero. If the rotors start at full speed, the starting power will be much greater than the power after the water is rotated at its equilibrium velocity. Drive motors should be oversized, therefore, or provision should be made to bring the paddles up to speed slowly during start-up(9).

7.3.3 Short Circuiting in Flocculation Reactors

As stated in preceeding sections, the degree of flocculation achieved within a basin is dependent on the magnitude of the mean velocity gradient, G, and the retention period in the basin. With the types of flocculation devices discussed in Section 7.3.2, in almost all cases (an exception, perhaps, is the baffled chamber) the action of the device gives rise to a certain degree of short circuiting in the basin. That is, some elements of liquid will leave the flocculation basin after a time less than the design retention period whereas others will remain for longer.

The degree of short circuiting may be determined by introducing a slug of tracer (eg. dye or salt) at the inlet to the basin and measuring its concentration, with time, t, at the outlet. If mixing within a tank is instantaneous, the concentration of tracer at the outlet, C, is given by(9):

$$C/Co = e^{-t/T} \tag{7.34}$$

where Co = initial concentration in the basin assuming instantaneous dispersion;
and T = design retention time of basin.

By carrying out experiments on a single basin with a moderate degree of mixing, Camp(9) found that experimental results correlated reasonably well with Equation 7.34. For different fractions of the nominal retention period, t/T, the respective percentages of tracer slug leaving the tank within a given time as predicted theoretically and measured experimentally were as follows: From integration of Equation 7.34, 22% of the slug theoretically leaves the tank within one-quarter the retention period; 40% in one half and 63% in a time equal to the retention period. Experimentally, the respective values were approximately 23%, 32% and 47%. From this it is seen that theoretically, only 37% of flocculating particles remain in the basin for the full design retention period under conditions of complete and instantaneous mixing. This short circuiting effect may be diminished with rotating devices by installing suitably designed stators i.e. by minimising the rolling factor, k, of the water. At the same time, uniform inlet and outlet conditions should be ensured. Kawamura(22) found that with inlet and outlet baffles, openings of 3 per cent of flow area minimised short circuiting. However, it should be noted that the flow through the openings should not give rise to velocity gradients greater than the mean value existing in the flocculation basin, otherwise breakup of previously formed floc will result (see Section 7.3.4).

The most effective means of minimising the effects of short circuiting is to install a number of flocculation reactors in series. This is the subject of the following section.

7.3.4 Compartmentalization

In Section 7.2.3 the progressively reduced total retention time for a flocculation system with increased number of flocculation basins in series was demonstrated.

The minimum possible retention period is achieved when the number of reactors in series is infinity, i.e. plug flow conditions. This phenomenon is of general occurrence when reaction kinetics are of first order, as is the case for orthokinetic flocculation.

A second beneficial effect of compartmentalization is to minimise the effects of short circuiting. Camp$^{(9)}$ presents an equation similar in form to Equation 7.34 describing the instantaneous dispersion curve for n compartments of equal size in series i.e.:

$$\frac{C}{Co} = \frac{n^n}{(n-1)!} \left(\frac{t}{T}\right)^{n-1} e^{-nt/T} \qquad (7.35)$$

where Co and T are based on the total volume of n tanks in series.

Figure 7.8 shows the dispersion curves produced by Equation 7.35. The area under a given curve at a particular time t represents the fraction of tracer slug which has passed through the system. Hence, integrating Equation 7.35:

Fraction of tracer slug passing through system in time t

$$= 1 - \frac{n^n e^{-(t/T)}}{n\,!} \left[\left(\frac{t}{T}\right)^{n-1} + \frac{(n-1)}{n} \left(\frac{t}{T}\right)^{n-2} + \frac{(n-1)(n-2)}{n^2} \left(\frac{t}{T}\right)^{n-3} + \right.$$

$$\left. + \ldots\ldots\ldots + \frac{(n-1)!}{n^{n-1}} \right] \qquad (7.36)$$

It is seen that as the number of compartments increases, the time of maximum response increasingly approaches the nominal retention time, T. For example, with three basins or compartments in series, 4% of a tracer slug will pass through the series within one-fourth the retention time and 19% of the slug within one-half the retention time. Note that with n = 10, C/Co is greater than 1,0 since Co is based on the total volume of the series.

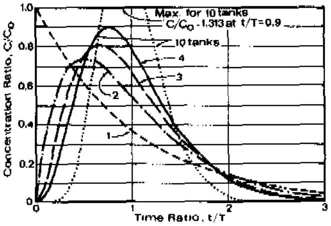
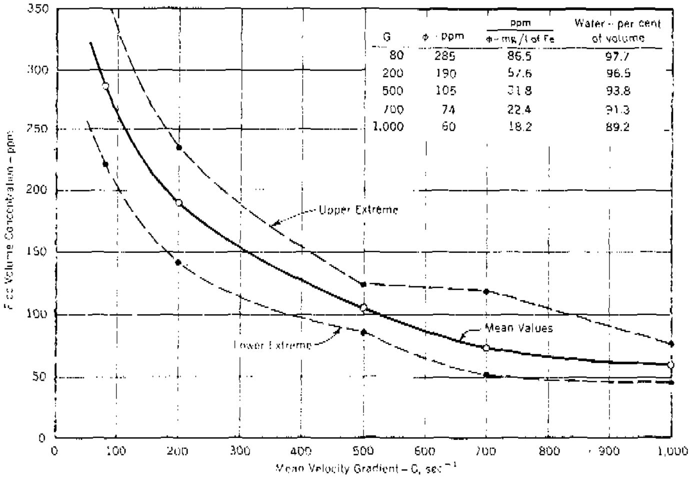


FIGURE 7.8: Dispersion Curves for Tanks in Series. (After Camp$^{(9)}$).

A further advantage of compartmentalization during flocculation is that a tapered velocity gradient through the system may be achieved. Camp$^{(10)}$ demonstrated that the higher the velocity gradients during flocculation, the lower is the floc volume concentration and, therefore, the more compact and less prone to shear disruption are the flocs. Camp's results for floc volume concentration for G values from 80 to 1000 s^{-1} are shown in Figure 7.9. It can be appreciated, from the foregoing, that by providing a high velocity gradient in the first chamber and subsequently lower velocity gradients in the second and third compartments etc., flocs with denser, more robust characteristics will be produced compared to a system where a single low G value is assigned to one or a series of tanks. A further beneficial effect realised with provision of a tapered velocity gradient is that, from a consideration of Equations 7.22 and 7.23, the total retention time for a series of reactors is further lowered when compared, again, with a series of reactors subjected to the same mean velocity gradient in each reactor. This latter aspect becomes more evident in the design example presented in Section 7.3.6.

The transfer of flocculating water from one compartment to the next, or of flocculated water from the final compartment to a sedimentation basin, must be carried out so as to prevent breakup of flocs already formed. Therefore, ports, conduits, baffles and so on must be designed such that at maximum expected flow, the mean velocity gradient during passage from one chamber to the next is at most no greater than the G value in the preceeding compartment. On the other hand, from a consideration of uniformity in flow pattern, the head loss through port orifices, conduits, baffles, etc., must be high with respect to the approaching velocity head and the number of openings should be as large as possible(18). As previously stated, Kawamura(22) recommends the ratio of openings to area of flow in each compartment in a plane perpendicular to direction of flow of 3% - with the proviso that velocity gradients are not excessive as explained above.



G	ϕ – ppm	$\frac{\text{ppm}}{\phi\text{ – mg/l of Fe}}$	Water – per cent of volume
80	285	86.5	97.7
200	190	57.6	96.5
500	105	31.8	93.8
700	74	22.4	91.3
1,000	60	18.2	89.2

FIGURE 7.9: Floc Volume Concentrations for 15 mg l^{-1} $Fe_2(SO_4)_3 \cdot 6H_2O$ in Tap Water at a pH 6,0 and After Rapid Mixing at Indicated G Values for 2 Minutes. (From Camp(10), With Permission of the American Water Works Association).

From the latter considerations, it is appreciated that considerations pertaining to minimising short circuiting, maintaining uniformity of flow and preventing floc breakup are inter-related and may in some cases be in conflict. Therefore, in design it is usually necessary to compromise the above factors.

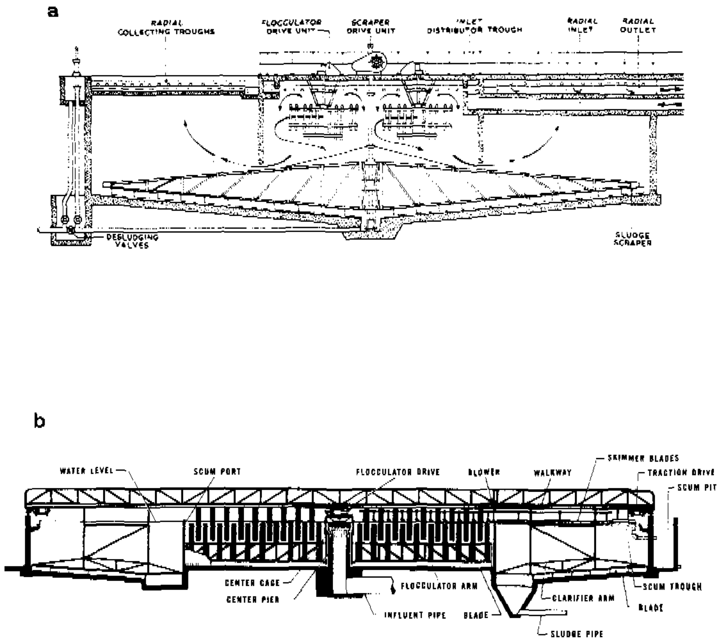


FIGURE 7.10: Examples of Combined Flocculation - Sedimentation Basins: (a) Centrifloc Clarifier (Courtesy Paterson Candy Int., Ltd.); (b) Clarifloccul-ator (Courtesy Dorr-Oliver).

7.3.5 Combined Flocculation - Sedimentation Basins

As mentioned in Section 7.3.4 a difficulty may arise when designing for the transfer of a flocculated suspension to a sedimentation unit. Although it should be possible to adequately size ports, conduits and so on, a further solution is to combine flocculation and sedimentation in one unit. Figures 7.10(a) and (b) illustrate two types of such combined units: (a) With the first unit, it is seen that neither compartmentalization nor a tapered velocity gradient are accomodated. As shown in the preceeding section provision of both these facilities is markedly beneficial. (b) With the second type, typical of larger units, the flow is horizontal and, therefore, a tapered velocity gradient may in principle be accomodated by appropriate design of paddle areas. However, as seen in Figure 7.10(b), paddles are often designed all of the same size which, theoretically, produces an increasing velocity gradient in the direction of flow (i.e. a *reverse* tapered velocity gradient profile). As an example, considering such a unit with seven equally spaced paddles of equal cross sectional area in a plane perpendicular to the direction of travel, and taking the volume swept by each paddle as a separate compartment, the ratio of the mean velocity gradient in the last compartment to the first compartment (i.e. considering successive compartments from the centre outwards in the direction of flow) is of the order 1:2. From this, one may suggest that with such units, a radial-peripheral feed-inward flow pattern would be preferable. With such an arrangement velocity gradients would be higher in earlier compartments, decreasing towards the centre. A further advantage of a peripheral feed unit would be the more uniform (converging) flow pattern set up. Short circuiting considerations for such combined units coincide with those for standard sedimentation basins. See, for example, Camp(8).

A disadvantage of the units described in this section, particularly with the larger types, is the possibility of settling occurring in the flocculation section thereby impeding the rate of flocculation. This would presumably be minimised in peripheral feed units where, as flocs are progressively formed, the velocity of flow accordingly increases. With centre-feed units, the velocity of flow decreases as floc formation proceeds.

7.3.5.1 Solids Contact Blanket Clarifiers

A special type of combined flocculation sedimentation device is the solids contact blanket clarifier, an example of which is shown in Figure 7.11. This device is widely used in the United Kingdom in the water treatment field as well as in several industrial applications.

The principal features of the solids contact blanket clarifier system are as follows (after Stevenson[40]):

(a) A rapid mixing system for coagulants;

(b) A delay period from the point of coagulant addition to entry to the clarifier;

(c) An inlet system to mix incoming water with preformed blanket floc, and to maintain the latter in stable suspension;

(d) A blanket or flocculation zone where primary floc particles formed during destabilization are filtered out and incorporated with preformed flocs;

(e) A supernatant clear water zone which serves primarily as a buffer to allow surges in blanket volume to be accomodated, and also to provide a degree of post flocculation;

(f) A clarified water decanting system;

(g) A blanket level control system (often carried out visually);

(h) A sludge concentrator, which may also serve as a level controller;

(i) A sludge bleed control.

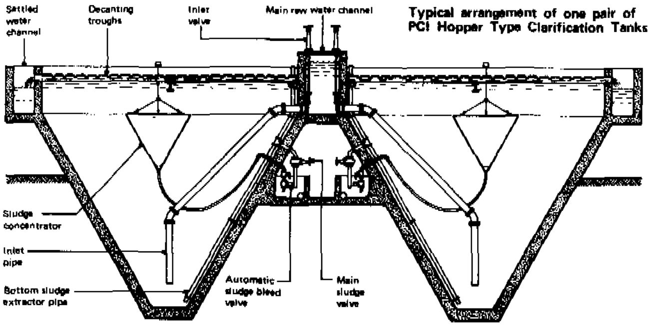
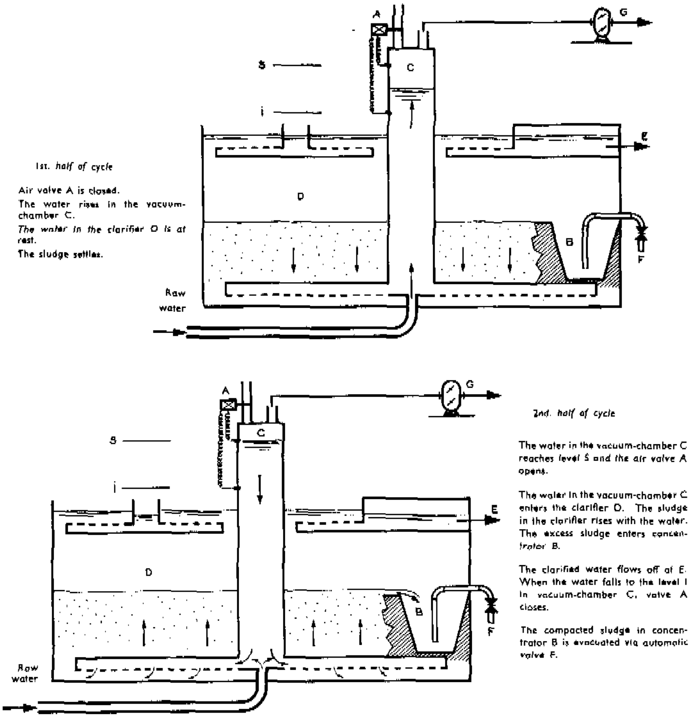


FIGURE 7.11: Example of Solids Contact Blanket Clarifier (Courtesy Paterson Candy, Int. Ltd.)

Figure 7.12 shows a variation of the blanket clarifier known as the Pulsator. Here, the mixing energy within the flocculating zone may be varied independently of the base flow. Approximately every four minutes a pulse of water is injected through the inlet at the bottom with the result that periodically the G values within the blanket are temporarily increased and then subsequently decreased. Furthermore, flocs settled on the floor of the clarifier are redispersed causing them to move upwards for reflocculation within the blanket.



1st. *half of cycle*

Air valve A is closed.

The water rises in the vacuum-chamber C.

The water in the clarifier D is at rest.

The sludge settles.

2nd. *half of cycle*

The water in the vacuum-chamber C reaches *level S and the air valve A* opens.

The water in the vacuum-chamber C enters the clarifier D. The sludge in the clarifier rises with the water. The excess sludge enters concentrator B.

The clarified water flows off at E. When the water falls to the level I in vacuum-chamber C, valve A closes.

The compacted sludge in concentrator B is evacuated via automatic valve F.

FIGURE 7.12: Principle of Operation of Pulsator (Courtesy Degrémont)

In general, the principle of operation of solids contact blanket clarifiers is that floc particles (formed within the clarifier) with a settling velocity greater than the surface overflow rate will be held in a position of equilibrium at some point where the upflow velocity relative to the particles equals the hindered settling velocity. Thereby, larger particles will form an equilibrium layer within which all smaller particles with lower settling velocities are trapped.

Solids concentration within the blanket increases with depth from the bottom with the highest concentration being at the top of the blanket. For floc blanket control and to minimize water withdrawal, sludge should be withdrawn from the top of the blanket. Calculating an exact sludge level is difficult and thus a sludge concentrator is normally positioned as near to the top of the blanket as possible. Concentrated sludge is thus withdrawn intermittently from the concentrator. Withdrawing sludge from a single opening in the wall is very unsatisfactory since a very watery sludge results and blanket control is difficult.

Instability of the sludge blanket, if it occurs, is principally due to two reasons: (a) poor inlet design, where the momentum of incoming water is not destroyed or, in the case of expanding units, boundary separation occurs. In the latter instance a practicable solution has been to install a series of baffles at the bottom of expanding flow units; (b) poor outlet design, where clarified water is collected unevenly from the top of the unit. To alleviate this, sufficient freeboard is usually provided above the top of the blanket. (As a rule-of-thumb, the freeboard depth should be approximately one half the distance between overflow weirs). Poor inlet and outlet conditions give rise to short circuiting and streaming with disturbance of the blanket surface and consequent floc carry-over with the effluent.

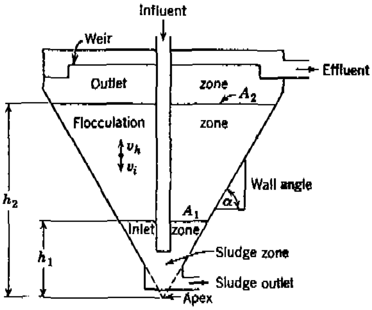


FIGURE 7.13: Vertical Section Through Conical or Pyramidal Upflow Tank (after Fair, Geyer and Okun[41]).

Referring to Figure 7.13 (after Fair, Geyer and Okun[41]), velocity gradients, G, existing in the sludge blanket are given by:

$$G = \{(\rho g/\mu)(s_s-1)(1-f_e)(h_2-h_1)/(C/Q)\}^{1/2}$$

Retention time within the blanket, or flocculating zone $= T = f_e C/Q$

where: g = gravity constant;
ρ = mass density of liquid;
μ = viscosity of liquid;
s_s = specific gravity of flocs;
f_e = relative pore space of flocculation zone;
h_2-h_1 = blanket or flocculation zone depth;
C = zonal volume or capacity;
and Q = rate of flow.

In assessing G at different depths within the blanket, values for h_2 and h_1 are taken as appropriate. In controlling G within the flocculation zone, f_e, h and C are the control variables and are selected to yield a desired floc growth rate and size. In design, a relatively high initial G value (at the bottom of the clarifier) is sought to promote floc growth. High G values at the top of the blanket are avoided to prevent floc breakup with subsequent loss over the effluent weirs.

7.3.6 Design Example

The following example demonstrates a suitable procedure for designing a flocculation system using data obtained from laboratory experiments. For the example it is assumed that a reciprocating blade type flocculator is to be used, although for other flocculation devices similar considerations apply. Furthermore, the design is carried out for one particular flow rate. Again, to accomodate a range of flow rates the procedure is basically the same. As will be seen from the example the minimum retention time to achieve the desired flocculation performance is determined. From this, the volume of the reactor system should be based on maximum flow conditions. With an in-series flocculation system it may be that at successively lower flows, operation of the first flocculation device may be discontinued, then the second and so on thereby economising power costs. However, with such a procedure, the velocity gradient profile determined for minimum possible retention time may not be suitable (i.e. too low in second and third compartments etc.) and may require adjustment. However, since now a retention time greater than the minimum possible will exist a balance must be made between increased capital cost of a larger flocculation system and decreased running (power) costs at lower flows. For such an analysis the treatment flow must be fully characterised and the frequency of occurrence and time span of particular lower flows identified. It is seen, therefore, that in such an analysis the procedure presented below will form the first step-being carried out for the maximum expected flow and identifying the mean velocity gradient profile yielding the lowest possible total retention time.

Batch flocculation tests carried out on a destabilized raw water (see Chapter 8) yield values for flocculation and breakup constants of $K_A = 2{,}5.10^{-4}$ and $K_B = (7{,}72 - 0{,}87 \ln G)10^{-7}$ s respectively. The turbidity of the raw water is 40 JTU and it is required that after flocculation and settling, the residual turbidity be not more than 2 JTU. Therefore, the desired flocculation performance is No/N = 20. The maximum expected flow to the treatment plant = $2\text{m}^3\ \text{s}^{-1}$.

For this design it is assumed that beyond a three compartment flocculation system, the savings in capital cost of smaller compartment sizes is offset by the cost of multiple stirrer mechanisms, baffles and so on. Furthermore, it is assumed that design and construction of the flocculation system will be more convenient if the three compartments in series are of the same size, even though G values will change from compartment to compartment.

A useful starting point is to assign equal velocity gradients to each of the three compartments thereby identifying the order of magnitude of velocity gradients giving lowest retention time. From a trial and error procedure and using Equation 7.23, for this example a velocity gradient of 20 assigned to each compartment results in a minimum retention time per compartment of 750s (i.e. 37,5 minutes for the whole system).

Using the G value and retention time computed above as an initial guide, various velocity gradient profiles may be systematically assessed using Equation 7.22. (Note that computation time is considerably reduced by using a programmable "pocket" calculator).

Using an initial total retention time of 1600s, the scheme of velocity gradient profile trials followed for this example were as shown in Table 7.2.

TABLE 7.2: Scheme of Velocity Gradient Profile Trials for Example

```
 80 - 40 - 20
          - 15 ← highest N0/Nm value (Eq. 7.22)
          - 10
_______________
    - 40 - 15
    - 50 -
    - 30 -     ←
    - 20 -
_______________
100 - 30 - 15
 80 -
 60 -
 75 -
 70 -
 72 -          ←
_______________
 72 - 30 - 15
    - 35 -
    - 25 -
    - 20 -
    - 24 -     ←
_______________
 72 - 24 - 15
          - 20
          - 10
          - 12 ← highest N0/Nm (= 20,59)
_______________
```

Fixing the most efficient velocity gradient profile of 72 - 24 - 12 s^{-1}, the retention time is varied and a minimum of 1530 s identified yielding No/N_m = 20,0.

From Equation 7.35, differentiating, equating to zero and rearranging, the effective retention time for a completely mixed system with n reactors in series is given by:

$$t = (n - 1)\, T/n \qquad (7.37)$$

where T = nominal retention time.

Therefore, for the present example, for an effective retention time of 1530 seconds, the nominal retention time, T, is given by T = 3.1530/2 = 2295 seconds.

Hence, volume per compartment = 2.2295/3 = 1530 m^3. Assuming the depth of compartments = 4m, superficial dimensions = 20m x 20m.

Assume the use of a reciprocating flocculation device, for example, of the type shown in Figure 7.7a.

Hence, length of blades = 20 - 4 = 16m.

Assume the blades are 50mm wide and spaced at 300mm centre to centre. Hence total paddle area = 20.16.0,05/0,3 = 52,8 m^2.

From Equations 7.6 and 7.33 and rearranging, the frequency of the blade stroke is given by

$$S_s = \left(\frac{G^2 V\mu}{6{,}58.10^3 C_D . D^3 \Sigma A}\right)^{1/3}$$

Hence, for the first compartment (and assuming a mean water temperature of 20°C):

$$S_s = \left(\frac{72^2 .1530.10^{-3}}{6{,}58.10^3 .3.4^3 .52{,}8}\right)^{1/3} = 0{,}0492\ s^{-1}$$

Hence time of travel of blade from the bottom of the first compartment, up to the water level and back to the bottom = 20s.

Assuming the same paddle configuration for the second and third compartments:

S_s (second compartment) = 0,024 s^{-1} and

S_s (third compartment) = 0,015 s^{-1}

Assume that dividing walls between compartments are provided with a number of circular ports and that the flow passes from the last compartment directly to a rectangular sedimentation basin. It is necessary to calculate the number and diameter of the ports such that the velocity gradient in the preceeding compartment is not exceeded. Furthermore, the head loss through the ports should be sufficiently high to assure uniformity of flow.

The head loss through each port is given by: $h_L = 8Q^2/(C_d^2\pi^2 d^4 g)$ where d = diameter of each port and Q = flow through each port.

The mean velocity gradient through each port is given by Equations 7.6 and 7.27 i.e. $G = (\gamma h_L/T\mu)^{1/2}$

Hence $$G = \left(\frac{8\gamma Q^2}{C_d^2\pi^2 d^4 g T\mu}\right)^{1/2} \qquad (7.38)$$

Basing the retention time, T, on 5 times the diameter of the port, $T = \frac{\pi d^2}{4}.5d/Q$. Hence, from Equation 7.38:

$$G = \left(\frac{0,021.\gamma.Q^3}{C_d^2\ d^7\mu}\right)^{1/2} \qquad (7.39)$$

Assuming a mean water temperature of 20°C:

$$G = \left(\frac{2,06.10^5 Q^3}{C_d^2\ d^7}\right)^{1/2}$$ from which

$$d = \left(\frac{2,06.10^5.Q^3}{G^2\ C_d^2}\right)^{1/7}$$

Assuming the number of ports = 16, flow through each = 2/16 = 0,13 $m^3\ s^{-1}$. Hence diameter of each port between the first and second compartments (where the mean velocity gradient in the first compartment = 72 s^{-1}) is given by:

$$d = \left(\frac{2,06.10^5.0,13^3}{72^2.0,6^2}\right)^{1/7} = 0,82m$$

where the coefficient of discharge, C_d, is assumed to be 0,6.

In a similar fashion, 16 - 1,10m and 16 - 1,34m diameter ports are calculated for dividing walls between the second and third compartments and between the third compartment and sedimentation basin respectively.

Note that although a rectangular sedimentation basin is assumed for this example, in principle the considerations are similar when circular basins are provided. In this case a number of pipelines (corresponding to the number of sedimentation basins) from the last compartment to the sedimentation basin(s) are provided with diameter such that, taking into account bends, entry losses and so on, the mean velocity gradient at no time exceeds that within the last compartment.

Taking the case of the smallest diameter ports between the first and second compartments, it is seen that the percentage of openings is 10% relative to the dividing wall nominal area; with the largest port diameters (between the third compartment and sedimentation basin) the percentage is 28%. These values are considerably greater than the figure of 3% recommended earlier. A solution is to alter the dimensions of the tank such that the width is considerably greater than the length and, furthermore, the flow is transverse to the flocculator blades. For this example, to achieve a 3% port area, the dimensions of the compartments in a plane parallel to the direction of flow would be of the order 5m long by 70m wide. In this case, construction of the flocculation system in a modular system (say 5) would be a feasible solution. A disadvantage, however, is the need for a much larger number of separate flocculation devices.

The above discussion demonstrates that, as stated previously, a number of conflicting factors may arise when designing a flocculation system. Although an attempt has been made in this example to demonstrate the nature of these factors, mediation in design needs to be carried out on the basis of the particular application.

7.4 CONTACT FLOCCULATION-DIRECT FILTRATION.

7.4.1 General

Although the filtration process does not strictly fall into the scope of this book, the particular process contact flocculation - direct filtration warrants inclusion. The reason is that with some waters, where the water quality is generally of a high standard, the process combination coagulation - flocculation - sedimentation and/or filtration may be inefficient. For dilute suspensions the flocculation process is kinetically poor and in such cases may, without operational modifications, be relatively ineffective.

With dilute suspensions, the most viable treatment alternative in several instances has been the contact flocculation - direct filtration process. In this process, raw water after destabilization is applied directly, or after a relatively short conditioning period, to a granular bed filter (see Figures 7.1c, d and e). Flocculation occurs during passage through the interstices of the media. The process accomplishes nothing that other perhaps more conventional processes can(12), but with some waters of appropriate raw water quality, the final water produced is of as high a standard, but with the advantage of significantly lower capital cost.

7.4.2 Appropriate Raw Water Quality

It was stated previously that direct filtration is often a more viable alternative than conventional flocculation - sedimentation for dilute suspensions. The reason is that unlike flocculation the transport efficiency, and thence the removal efficiency during filtration is independent of particle concentration(14) under correct operating conditions. However, in terms of operational considerations, too high a suspended material load during direct filtration will result in impracticably short filter runs before breakthrough. For this reason there is an upper limit to water constituents beyond which the use of direct filtration is precluded. The following presents an initial guide to the appropriate water quality for the consideration of direct filtration.

In general(12) (a) the raw water turbidity and colour should each be less than 25 units (JTU or FTU) or (b) if the colour is low, the maximum turbidity should not exceed 200 units or (c) if the turbidity is low, the maximum colour should not exceed 100 units. Some workers(23), however, limit raw water turbidity to 5 to 10 turbidity units, stating that with average turbidities exceeding this value direct filtration may become inefficient due to short filter runs and filter breakthrough. If paper fibres or diatoms are present in the water, concentrations in excess of 1000 asu ml^{-1} (areal standard units per millilitre) have a marked influence on the length of filter runs and require the inclusion of sedimentation before filtration(12, 19). Furthermore, diatom levels in excess of 200 asu ml^{-1} may require the use of coarse media for the top layers of the bed to achieve adequate filter runs. Coliform MPN's of up to 90 per 100 ml appear to have been handled satisfactorily(12) by direct filtration and there seems to be little reason to assume that significantly higher levels should not also be satisfactorily handled.

In the case of direct filtration applied to secondary effluents with the objective of phosphorus precipitation and removal, a rough guide(21) is that for run lengths in excess of 6 hours and less than 10 per cent backwash water, the upper limit to suspended solids concentration is 50 mg TSS l^{-1} with a phosphorus concentration of 3 to 4 mg l^{-1} as P.

Although *a priori* consideration, as above, may be given to the possibility of using a particular direct filtration process, the precise configuration of the most suitable process (from options (a) to (e) in Fig. 7.1) may only be decided after pilot plant trials have been carried out using the particular raw water. A thorough account of the procedures for carrying out pilot scale filtration experiments has been presented by Ives(20).

7.4.3 Advantages and Disadvantages

The principal advantage of a direct filtration facility over other processes is that, in cases where the raw water quality is appropriate, cost savings of up to 30 to 35%(12, 36) compared to conventional processes may result.

The cost saving arises principally from the elimination of flocculation facilities and/or sedimentation facilities.

Savings in chemical costs of up to 10 - 30 per cent(12) may also be realised using direct filtration since less coagulant is required compared to that necessary to produce a settleable floc. Although flocculant aid dosages (if used) may in some cases be greater, the higher associated cost is usually offset by lower primary coagulant costs.

Further advantages are that operation and maintenance costs are reduced (because there is less equipment required) and waste solids are all contained in a single strea (the filter backwash) thereby facilitating treatment.

Disadvantages are that filter runs are generally shorter in direct filtration compared to filtration preceeded by settling. Although the cost consequences of this may not be too significant, operational problems may result in some cases. Backwash water usage is also generally higher with direct filtration; often as high as 6 per cent compared to a total of 4 per cent total waste sludge from a conventional process (comprising 2 per cent for backwash plus 2 per cent for sludge wastage). However, this difference may not be significant in terms of operating costs(12).

Perhaps the principal potential disadvantage with direct filtration is the short time lag between coagulant addition and filtration requiring a higher standard of control or operator vigilance(32). However, the inclusion of a control filter and contact (or retention) basin prior to filtration may effectively overcome this difficulty. Because of this, and considering that the capital cost of a contact basin would be much less than that of a settling basin, inclusion of such a facility in a direct filtration scheme has been strongly recommended(12).

7.4.4 Mechanisms

In direct filtration, suspended material in the raw water is destabilized by the addition of coagulant chemicals and passed directly to a granular bed. Because of the high velocity gradients generated during passage through the interstices, contact flocculation takes place at a rate much higher than normally afforded on average during the conventional flocculation process. Floc particles, which at this stage are of minute size, become attached or adsorbed to the surface of filter grains. The smaller the filter grains, the higher is the rate of contact flocculation and the higher is the total surface area provided for attachment. The extent and manner of particle removal within the filter far exceeds that which may be accounted for solely by a straining action (12) which indicates the influence of physical - chemical parameters. Pores of the filter gradually fill with particles throughout the depth as flocs progressively grow in upper layers of the bed, become unstable, are sheared off and pass down through the bed. Finally, either the head loss in the bed increases to the maximum allowable or breakthrough of particles appears in the filtrate, either event requiring cessation of operation and backwash.

Removal of suspended matter within a filter bed may be considered to occur in two separate and distinct steps(23, 25, 27): (a) a transport step and (b) an attachment step.

7.4.4.1 *Transport*

The transport stage consists of removal of suspended particles from the hydraulic stream and bringing them close to the surface of grains or existing deposits in the bed. Transport depends on *physicohydraulic* factors(1). Such factors include interception, settling, diffusion and hydrodynamic forces. It is argued whether the additional mechanism of intersticial straining forms part of the transport or attachment stage. The influence of the above factors depends on the diameter of the granular media and of the suspended material, the rate of filtration, the viscosity of the liquid and density of suspended particles. With direct filtration where a pre-flocculation facility is not provided, flocculation occurs to a certain extent during the transport step. The presence of large flocs formed within interstices of the bed is experimentally evident(31); however, the relative influence of orthokinetic flocculation during transport or subsequent growth on the media after attachment is not known. The transport step during filtration is analogous to the orthokinetic flocculation stage during the conventional flocculation process(27, 33).

7.4.4.2 *Attachment*

Attachment of suspended particles to the grain surfaces or to existing deposits is controlled by the surface properties of the respective materials. The process of attachment is analogous to that of destabilization in the coagulation process(27, 33). Two mechanisms describing attachment are (a) double layer interactions and (b) specific chemical interactions. With the double layer theory it is assumed that interaction between a suspended particle and media surface can be described by a combination of Van der Waals attraction with the coulombic attraction or repulsion of the double layers. However, O'Melia and Stumm(27) state that although electrostatic interactions are significant, they probably do not solely control attachment. For an understanding of the attachment step during filtration it is necessary to consider an analogy with particle destabilization where both electrostatic interactions and chemical interactions are of importance (see Chapter 4). Here, rather than particle - particle interactions, one thinks in terms of media surface (which includes already attached material) - particle interactions. With a consideration of the foregoing, the influence of pre-conditioning the filter media and destabilization of suspended material may readily be appreciated. Furthermore, the lag period or working - in period of the filter after backwashing is also understood.

7.4.5 Design and Operational Aspects

7.4.5.1 *Media Characteristics*

Filter media considerations for direct filtration are basically the same as for filtration preceeded by settling. However, the use of single media sand filters is not recommended(12) especially for normal direct filtration rates of 10 - 18 $m^3\ m^{-2}\ h^{-1}$. The use of downflow dual-media (e.g. anthracite and sand)or mixed-media (e.g. anthracite, sand and garnet) is more appropriate(12, 19, 21, 23, 31, 36).

In selecting media size, the finest media concomitant with appreciable filter runs should be selected from pilot plant trials. This serves to minimise polymer dosages. With coarse filter media the higher shear intensities require higher polymer dosages to increase the shear strength of flocs.

Culp(12) gives two examples of filter media appropriate for direct filtration: (a) a four media 91 cm bed comprising

(i) 41 cm of -4- +14 mesh coal (i.e. passing ±4,5 mm, retained on 1,41mm sieve) specific gravity 1,48;
(ii) 20 cm of -9- +18 (2,2 - 1,0mm) mesh coal, specific gravity 1,62;
(iii) 20 cm of -30- +40 (0,59 - 0,42mm) mesh sand, specific gravity 2,4 and
(iv) 8 cm of 40 - 80 (0,42 - 0,177 mm) mesh garnet, specific gravity 4,2.

(b) a dual media 91 cm bed comprising
(i) 64 cm of -4- +20 (4,5mm - 0,84mm) mesh coal, specific gravity 1,55 and
(ii) 28 cm of -20- +50 (4,5mm - 0,297mm) mesh sand, specific gravity 2,4.

The dual media bed (b) will produce the same effluent quality as the multi-media bed but at the expense of higher chemical dosages and shorter filter runs.

Kavanaugh _et al_(21), testing various filter media characteristics for direct filtration applied to tertiary phosphorus and suspended solids removal (3-4 mg l^{-1} P and 50 mg TSS l^{-1} respectively) found a three-media filter superior to dual media filters. Characteristics of the three media type are as follows:

20 cm of 0,5-1,2 mm sand;
40 cm of 1,5-2,5 mm coal and
65 cm of 1,5-2,5 mm pumice

Shea et al(31) investigating several types of media for direct filtration applied to a synthetic water with clay turbidity, found that a coarse and uniform dual media bed gave superior results to a fine well graded dual media bed which, in turn, was superior to a single media sand filter. The characteristics of the first filter are as follows:

40 cm of coal, effective size (ES) 2,5 mm and uniformity coefficient (UC) 1,32.

15 cm of sand, ES 1,1 mm and UC 1,23.

Hutchison and Foley(19) showed that with direct filtration applied to waters where diatom levels may be a problem, by using dual media filters (45 cm coal plus 30 cm sand) where the coal layer ES is greater than 1,5 mm, diatoms up to 2500 asu ml^{-1} with filter runs exceeding 12 hours at 12 $m\ h^{-1}$ can be accomodated. In the absence of diatoms, the coal size may be reduced to an ES of 1,0 to 1,1 mm.

7.4.5.2 Coagulant Addition

There are essentially three alternative configurations of coagulant addition: the first is metal coagulant alone, added during rapid mixing and passed either directly or via a contact basin to the filter; the second is metal coagulant added as above but with a flocculant aid added (e.g. non-ionic polyelectrolyte or activated silica) just before filtration and the third is metal coagulant eliminated and replaced with, usually, a cationic polyelectrolyte serving as primary coagulant. In a discussion to the relative merits of the above alternatives, it is necessary to review the removal process during filtration. The removal process comprises three stages: a working-in stage, a working stage and a breakthrough stage(1). During the working - in stage the turbidity of the filtered water decreases rapidly until it reaches a stable low value. The presence of the working - - in stage indicates that for efficient attachment, floc particles must provide an initial coating of the media. The working - in stage is usually shorter when using metal coagulant rather than polyelectrolyte as primary coagulant(1). The working stage, considered to commence when the working -

in stage produces a stable low value, is the main phase during filtration. During this stage, polyelectrolytes produce a better effluent quality for all depths than metal coagulant. For the same operating conditions, therefore, the use of polyelectrolyte is more efficient than metal coagulants in terms of removal ability.

If the filter run is subsequently not terminated for reasons of head loss, the filtrate turbidity begins to rise which indicates the breakthrough stage. The onset of breakthrough is usually faster using metal coagulant than polymer.

Although the implication above has been the superiority of polyelectrolyte usage over metal coagulant, a disadvantage is that with beds of conventional grain size, polyelectrolytes produce a rapid head-loss increase which drastically shortens the cycle time. This may be overcome, however, by combining polymer usage with a coarse bed filter thus increasing the output. This latter combination is reported(1) to be superior to alum, say, and the use of a medium bed. In some instances, it is necessary to use metal coagulant to obtain efficient removal of water constituents. In this case the same discussion as above applies to the use of polyelectrolyte as flocculant aid. In the case of direct filtration applied to tertiary phosphorus removal(21), appreciable run lengths may not be achieved without the addition of, say, a non-ionic polyelectrolyte as flocculant aid. For this application, Kavanaugh _et al_ used ferric chloride as precipitant with an Fe: P ratio of 1,5.

The reason for the inferior results often evident using metal coagulant alone during direct filtration is that metal hydroxide flocs suffer lack of floc compressibility within the filter bed. Furthermore, there is a proportional relationship between floc volume and metal coagulant dosage. For these reasons, an almost inversely proportional relationship between the length of filter runs and metal coagulant dose has been reported(19). However, the metal coagulant dose for direct filtration is normally much lower than for cases where sedimentation is included before filtration. For example, in one case with a water of turbidity

80 FTU, the optimum alum dosage for direct filtration was 5 to 9,5 mg l^{-1}. Jar test results however (reflecting the dosage required for settling) predicted a dosage of 35 mg l^{-1} (23).

As mentioned previously, when polyelectrolytes are used as flocculant (or filter) aids in conjunction with metal coagulants, a nonionic or slightly anionic polyelectrolyte is usually best. Dosages reportedly range from 0,05 to 0,5 mg l^{-1} (12). When polymers are used as primary coagulants, a cationic polymer is usually required at dosages reportedly ranging from 0,1 to 5 mg l^{-1}. The combined cost of metal coagulant plus flocculant aid is usually less than using cationic (primary coagulant) polymer alone although this depends on the raw water quality. In some instances, especially in waters with relatively high concentrations of *divalent cations* (*e.g.* Ca^{++} and Mg^{++}) anionic or nonionic polymers may serve adequately as primary coagulants(25). Cationic polymer types, however, rely to a much lesser extent on the presence of cations and hence, for very soft waters, cationic polymers probably produce better results as primary coagulants. The influence of divalent cations is probably to either facilitate a bridging attachment of polymer to bed media and suspended particles or to modify the polymer conformation so as to improve adsorption. Loganathan and Maier (25) suggested that in their experiments, *although the* adsorption of anionic polymer was only about one-tenth that of non-ionic and cationic types, the higher efficiency of turbidity removal in the presence of divalent cations was because the anionic polymer, being weakly bonded to the sand, physically extends more into the interstices and thereby promotes removal by enmeshing particulate material.

7.4.5.2.1 Optimising Coagulant Dosage During Filter Operation

During initial filter operation, where polyelectrolytes are used as flocculant aids with metal coagulants for the purpose of pre-conditioning the filter media, an excess of polyelectrolyte should be added. In order to optimise coagulant and polyelectrolyte dosages, the following method(12) may be used: (a) initially set the dosage of polyelectrolyte to metal coagulant at 1:40; (b) adjust coagulant dosage until the limiting filtrate quality is obtained; (c) after optimising metal coagulant dosage as in (b), reduce polyelectrolyte feed until breakthrough occurs just before maximum head loss is achieved. A slight increase in the polyelectrolyte dosage thus determined ensures that maximum head loss occurs before breakthrough during operation.

It should be emphasised at this stage that although the conventional jar test technique (see Section 8.1) may in some cases identify optimal chemical conditions for direct filtration(1), the floc requirements for this process and one in which sedimentation precedes the filter are, in general, different. For settling, a large, dense floc is required whereas with direct filtration a strong, pinpoint floc is required which has the capacity to resist the high shear forces in the filter, occupies less space, encourages longer runs and delays breakthrough. From these comments it is seen that in certain cases of raw water quality, flocculation prior to filtration may not only be unnecessary but also undesirable. Furthermore, the efficiency of rapid mixing (Chapter 6) has as great an importance, if not more so, than when followed by a flocculation basin.

7.4.5.3 Filter Operation

Although filter rates as high as 20 m h^{-1} have been reported(1, 12), a design rate usually recommended for reverse graded filters is 10 m h^{-1} (12, 23, 34, 36). This provides adequate safeguard to variations in raw water quality and allows flexibility of operation. Influent and effluent piping to the filter should be designed for 25 m h^{-1}. Backwash rates range from 36 to 58 m h^{-1}(12), the higher figures being applicable to raw waters with high plankton loads. Surface wash or air scour is strongly recommended for direct filtration (12, 30), especially for waters with high concentrations of iron; when sewage effluents are treated or when polyelectrolytes are used in the process.

Optimisation of filter operation occurs when the two design parameters t_1 (time to reach breakthrough) and t_2 (time to use available hydraulic head) are equal. The two parameters t_1 and t_2 depend on the mass and volume concentration of the suspension, floc strength and size distribution, media design and filtration rate. The average times of filter runs range from 5 hours up to 100 hours(12). Under the poorest raw water conditions short runs of 8 hours are tolerable in municipal plants although in some industrial applications, runs as low as 2 hours are acceptable. At the end of the filter run, breakthrough should not have occurred prior to maximum head loss being achieved. Many water treatment plants employing direct filtration allow a maximum head loss ranging from 1 to 2m. Figure 7.14(21) shows a schematic representation of the dependence on medium size and filtration rate of run time in terms of t_1 and t_2. The condition of $t_1 = t_2$ is shown. It is seen that at a given filtration rate, t_1 decreases as the medium size increases while t_2 increases with increasing medium size. t_1 and t_2 intersect at a particular optimum medium size which is dependent on the flow rate.

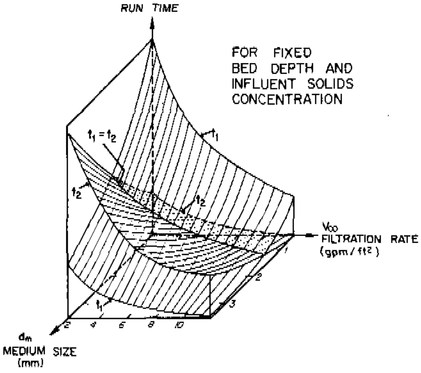


FIGURE 7.14: Effect of Filtration Rate and Medium Size on t_1 and t_2 for a Given Bed Depth and Influent Solids Concentration ($gpm/ft^2 \times 0{,}67902 = 1\ m^2\ s^{-1}$). (From Kavanaugh et al(21), with permission of the Water Pollution Control Federation).

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8

Coagulation and Flocculation Tests

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8.0 INTRODUCTION

The efficiency of the coagulation-flocculation process is dependent on many variables. For a particular water these include: (i) type of coagulant used; (ii) coagulant dosage; (iii) final pH; (iv) coagulant feed concentration; (v) type and dosage of chemical additives other than primary coagulant (e.g. polyelectrolytes, etc.); (vi) sequence of chemical addition and time lag between dosing points; (vii) intensity and duration of mixing at rapid mix stage; (viii) type of rapid mix device; (ix) velocity gradients applied during flocculation stage; (x) flocculator retention time; (xi) type of stirring device used and (xii) flocculator geometry.

To adequately assess the optimum conditions for the overall process it is necessary to use a testing procedure which sequentially maintains each parameter constant while the optimum value of a particular parameter is determined.

The pre-requisite for such a series of tests is, if possible, to thoroughly analyse the water and thereby identify the impurities most requiring consideration. In many cases the impurities of major concern are colour and/or turbidity, but in others residual phosphorus, iron, viruses and so on may be the governing criterion. The particular application obviously decides the desired final water quality and, therefore, the combination of coagulation-flocculation variables most appropriate. In some instances, tests must be carried out on a water or wastewater with unknown characteristics. Although an *a priori* estimation of the likely range of process variables in such cases is not possible, the testing procedure remains essentially the same. With some applications final effluent quality is not of major importance; an example is with sludge conditioning where the specific resistance or capillary suction time of the sludge after treatment is of concern.

A word of caution is appropriate at this stage. When following the treatment presented in this and perhaps earlier chapters, there may be a danger of gaining the impression that waters to which the coagulation and flocculation process is applied have well defined properties requiring pre-analysis only and fixation of design parameters on this basis. In practice most waters, especially from natural sources, are seasonally variable and, therefore, require testing during all changes in water quality. Plant design should naturally be based on the variation in water quality rather than on one set of data obtained at one particular time.

8.1 OPTIMIZING PRIMARY COAGULANT TYPE, DOSAGE AND pH

8.1.1 General

The starting point in a series of tests serving to characterise a particular water in terms of coagulation/flocculation performance is to determine the type of primary coagulant, its optimum dosage and the pH at which it operates most efficiently. The following sections describe the apparatus, methodology and considerations leading to a satisfactory test procedure.

8.1.2 Apparatus

The apparatus used for assessing the performance of a particular primary coagulant is the standard jar test apparatus, an example of which is shown in Figure 8.1. It consists essentially of a rack of stirrers, driven by one motor, under which 600 ml, or preferably 1 litre glass beakers are arranged. Beakers of lesser capacity than 600ml should not be used since irreproducible results may occur due to difficulties in accurately adding coagulants or coagulant aids. Furthermore, where the test criterion is settling velocity, tall beakers of large capacity are to be preferred. A further factor supporting the use of beakers of large capacity was pointed out by Habibian and O'Melia(11): when using polyelectrolytes either as primary coagulants or coagulant aids, the inner surfaces of the beakers serve as adsorption sites for the polymer. The effect is accentuated when smaller beakers are used and for waters of low turbidities where the total colloidal surface area may be of the same order of magnitude as the beaker inner surface area. For this reason beakers of at least 1l capacity are recommended.

The speed of rotation of the stirrers on the jar test apparatus is variable using, in almost all cases of proprietary equipment, a thyristor speed control connected to the motor. A variable speed facility is required because a fast speed is used during coagulant addition and a slow speed for the flocculation phase. Speed variation using a thyristor control (which varies the speed of the motor) is perhaps not the best method since the speed is often not exactly reproducible at a particular dial setting. More satisfactory is a constant speed motor with some form of gear or pulley arrangement.

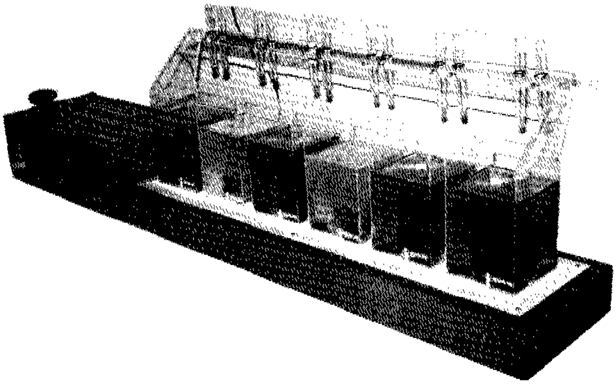

FIGURE 8.1: Example of Jar Test Bench Stirring Apparatus. This Particular Model Incorporates a Constant Speed Motor to Which is Directly Coupled a Drive Wheel. Speed Control is Effected by Altering The Position of the Drive Wheel on a Second Larger Whee Coupled to a Series of Rotating Magnets, Which In Turn Drive the Impellers Within the 2 Litre Sample Jars. A Rack of Chemical Dosing Tubes Situated Above the Jars (Two For Each) Effect Simultaneous Chemical Addition to All Six Samples. (Courtesy Induslab, Brasil)

Further desirable features of the apparatus are (i) a light source arranged either above or below the beakers (e.g. a daylight 'cold' fluorescent tube). A black background to the beakers is also useful; (ii) flat bladed stirrers rather than the propellor type; (iii) a rack of, for example, test tubes spaced so as to coincide with the position of the beakers and thus facilitate simultaneous chemical addition. Addition of coagulant should be rapid and the stirring should be such that dispersion occurs in as short a time as possible.

8.1.3 Chemical Solutions

Stock solutions of each coagulant or coagulant aid etc. to be used are prepared such that the volumes corresponding to the dosages to be used may be accurately and conveniently measured. It is convenient to prepare each coagulant (if a series of metal coagulants are to be tested) at the same concentration expressed as the metal ion. For example, 500 mg l^{-1} as the metal ion corresponds to a stock solution concentration of alum $Al_2(SO_4)_3.16H_2O$, of 5,8333 g l^{-1} and of ferric sulphate, $Fe_2(SO_4)_3.9H_2O$ of 2,5089 g l^{-1}. Using analytical grade reagents in the laboratory, the corresponding commercial coagulant concentrations may be determined from the percentage of metal ion given by the manufacturer. For routine monitoring of plant performance, madeup chemical from the plant may be used, suitably diluted to, say, 5 g l^{-1} as alum or ferric sulphate etc. Using stock solutions as given above, i.e. 500 mg l^{-1} as Al or Fe, or, 5 g l^{-1} as alum or ferric sulphate etc. lends convenience when adding coagulant to 500 ml or 1 l beakers. For example, with a stock solution of 500 mg l^{-1} as Al and using 500 ml samples, 10 ml of stock solution corresponds to a concentration of added coagulant of 10 mg l^{-1}. Using 1 l samples the concentration would be 5 mg l^{-1}. For this latter case it is convenient to double the stock solution concentration such that, again, 10 ml added to 1 l corresponds to 10 mg l^{-1}.

The keeping properties of chemical solutions depend principally on the chemical and the concentration. For example, for a 10 g l^{-1} alum concentration, the solution may be used up to one month. For the same concentration of ferric sulphate, solutions should not be used for longer than one week. If the solutions become opalescent before this time, they should be renewed. Sulphûric acid and sodium hydroxide solutions of 0,1 N should be renewed after 3 and 1 month respectively. With coagulant aids it is best to refer to the manufacturers' literature. As an indication however, a 0,05% stock solution of a polyacrylamide derivative should not be used for longer than approximately one week and should be at least 1 day old before use. Prior to each day's testing program, sufficient quantity of polyacrylamide stock solution should be diluted to at least 0,005%.

8.1.4 Criteria Describing Process Performance

Before coagulation/flocculation tests are carried out it is necessary to decide which criterion (or criteria) of process efficiency is the most appropriate for the particular water under test and for the existing or proposed method of treatment (i.e. sedimentation, filtration etc.). The most common criterion is to take supernatant samples after a given period of settling and analyse for residual turbidity, colour, iron etc. as discussed earlier.

However, as the following list shows(3, 17, 19, 20), the evaluation of optimum coagulant type, dosage and pH using the jar test procedure may be carried out on the basis of a wide variety of criteria; the applicability of each dependent on the particular process used after coagulation:

(i) Settling and assessing supernatant quality;
(ii) Filtration through a small granular bed filter and assessing filtrate quality;
(iii) Determining the time from coagulant addition to the first appearance of a visible floc;
(iv) Visually recording or comparing flocs as they are formed;
(v) Floc density measurements;
(vi) Floc volume concentrations determined by removing samples from the jar test apparatus and manually counting and sizing the particles using a stereo-microscope;
(vii) Volume of settled floc;
(viii) Residual coagulant concentration;
(ix) Silting index using a 0,45 μ membrane filter at constant pressure where silting index, S.I., is given by

$$SI = \frac{\text{Time to filter 2nd 5 ml sample} - \text{Time to filter 1st 5 ml sample}}{\text{Time to filter 1st 1 ml sample}}$$

(x) Filtrability number, which is the ratio of the time to filter 200 ml of jar test supernatant through a 0,45 μ membrane filter, to the time required to filter an equal volume of distilled water.

(xi) Membrane Refiltration which involves the formation of a filter cake by passing the jar test suspension through a 0,45μ membrane filter under constant pressure. The filtrate is collected and refiltered through the cake and membrane, the time required to refilter a specified volume being recorded.

(xii) Inverted gauze filtration;
(xiii) Cation exchange capacity;
(xiv) Surface area concentration;
(xv) Conductivity;
(xvi) Zeta potential;
(xvii) Streaming current detection;
(xviii) Colloid titration;
(xix) Cotton plug filters;
(xx) Electronic particle counting;
(xxi) Specific resistance;
(xxii) Capillary suction time, and so on.

TeKippe and Ham(19, 20) selected a number of the above criteria and evaluated their respective merits. They formed groups of three categories; those based on colloidal charge reduction (e.g. colloid titration); those measuring floc settleability (e.g. conventional-settled-jar test; floc formation time test; visual floc size comparisons and electronic particle counting); and those measuring floc filtrability (e.g. membrane refiltration).

For the suspension used by them the colloid titration technique was found to be of little use in determining an optimum coagulant concentration. For the category of settleability the conventional jar test was found to be the most reliable or practicable. Electronic particle counting, although a useful laboratory research tool and a more sensitive measuring technique than nephelometry or turbidimetry(4) cannot replace the conventional jar test for the control of existing or optimisation of dosages for new water treatment plants.

The results for the technique of membrane refiltration were found to correlate well with pilot scale filter experiments. Although not a useful technique in cases where the settleability of a suspension is of importance, it may be recommended for design of coagulant type, dosage and pH or control of plants which rely heavily on rapid sand filtration or diatomite filtration. Shortcomings of the test are that, firstly, it does not indicate the clarity of the filtrate(12) and, secondly, in the use of multi-media filters, where the formation of a compressible cake is minimised, the technique may not predict actual performance(20).

It should be emphasised at this stage that the optimum coagulant dosage for direct filtration may be much lower in some cases (especially for low turbid or coloured waters) than for settling requirements. However, it has been reported that settled jar test results predict closely optimum dosage requirements during filtration. For example, Adin and Rebhun(1) using a cationic polymer as primary coagulant found the same optimum dosage for both settling and filtration (see Figure 8.2). The filtration apparatus used by them to optimise dosage comprised sand filters 50 and 150 mm in length. TeKippe and Ham(19, 20) showed that filters of such size do correlate well with jar test settling results but not necessarily with larger pilot or full scale filters. However, Habibian and O'Melia(14), using polyelectrolytes as primary coagulants, found that conventional jar test (settling) results correlated well with large scale pilot filtration results, provided the error attributed to using small capacity beakers was eliminated, as explained earlier.

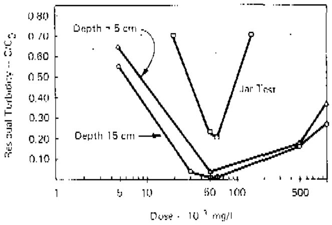

FIGURE 8.2: Results From Jar Test (Settling) Experiments and Small Scale Granular Filters Give Same Optimum Coagulant Dosage Conditions. (From Adin and Rebhun(1), With Permission of the American Water Works Association).

From the preceeding discussions, in the initial investigations for the design of a water treatment facility where the jar test is carried out to assess optimum coagulant conditions, it is probably expedient to assess both settling (conventional jar test) and filtration (membrane refiltration). A fairly reliable indication will thereby be achieved of the likely range of conditions using, say, conventional treatment utilising sedimentation or, say, direct filtration. The two techniques, settling in the conventional jar test and membrane refiltration, are described in the following section.

8.1.5 Jar Test Procedure

Whichever criterion of destabilization efficiency is chosen, the experimental procedure remains essentially the same and is set out below. As described earlier, stock solutions of each coagulant to be tested are prepared, each at the same concentration as the metal ion e.g. 500 mg l^{-1} as Al or Fe. A 500 ml or 1000 ml sample (depending on the apparatus available) is placed on the bench stirrer and the impeller speed set to *maximum*. It is convenient to run each batch of tests at a constant coagulant dosage. Each sample, therefore, for a particular test run is dosed with acid or alkaline regent ($Ca(OH)_2$ or NaOH etc.) to produce a range of pH values. For example, for a jar test apparatus accomodating 6 samples simultaneously, the initial pH is each may be adjusted to 4; 5; 6; 7; 8 and 9 respectively, using a pH electrode immersed in the sample. Maintaining the impellers at the fast speed, coagulant is then added using the rack of containers (e.g. test tubes) so that coagulant addition is rapid and dispersion virtually instantaneous. The necessity for the latter procedure is apparent if one considers the scheme of chemical addition in practice. The pH recorded as operative for a particular test is the final pH after coagulant addition. It should be noted that post adjustment of pH after coagulant addition to some pre-determined value is not valid since destabilization reactions are usually not reversible.

On adding the coagulant a stop clock/watch should be started and the fast rate of stirring continued for a set period (the same in the whole series of tests for the particular water). A satisfactory *rapid mix time* is 1 minute. After this period set the stirrers to slow speed. A satisfactory speed should be pre-determined by trial and error. A guide is that the speed should be slightly greater than the minimum required to maintain flocs in suspension. This speed, once determined for the particular water under test, should be used for the whole series of tests. After slow stirring for 14 minutes, say, the stirrers are stopped. Depending on the criterion of destabilization/flocculation efficiency deemed to be the most appropriate, the samples are allowed to settle in the jars for 15 to 30 minutes, or the sample filtered immediately, and so on.

In cases where settling is the criterion of interest the procedure is as follows. After switching off the stirrers, the samples are allowed to stand for a set period of, say, 15 minutes (again, the same for the whole series). After settling, a supernatant sample is taken horizontally from each jar using a pipette, the end of which is bent through 90°. The supernatant sample is taken at a constant depth of 30 mm. The supernatant samples are then analysed for whatever criterion or criteria of effluent quality is the most appropriate, for example, residual turbidity, colour, phosphorus etc. In the case of turbidity measurements, greater reproducibility may be attained by adding, say, one drop of concentrated reagent grade hydrochloric acid per 100 ml of supernatant sample (to reduce the pH to ± 2,5(2)) and vigorously shaking the sample. This procedure reduces the effect of particle size on residual turbidity measurements.

In cases where filtration is of interest, the membrane refiltration procedure mentioned earlier is probably of the most practicable interest. The procedure is as follows: Figure 8.3 shows the apparatus used by TeKippe and Ham. A 250 ml sample is taken immediately after the slow mix period and filtered through a 0,45 μ membrane filter under a vacuum of 100 mm Hg. Approximately 100 ml of the filtrate is collected and refiltered through the cake and membrane and collected in a 100 ml cylinder. The time taken to filter 80 ml of filtrate; i.e. from the 10 ml to 90 ml mark on the graduated cylinder, is recorded as refiltration time.

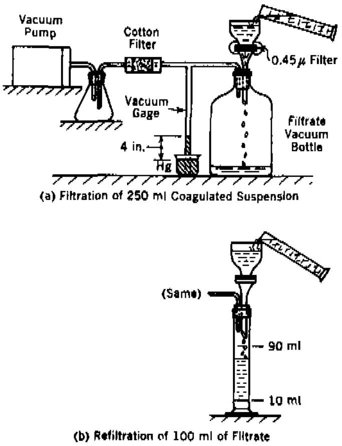

FIGURE 8.3: Apparatus for Refiltration Experiments. (From TeKippe and Ham$^{(19, 20)}$, With Permission of the American Water Works Association).

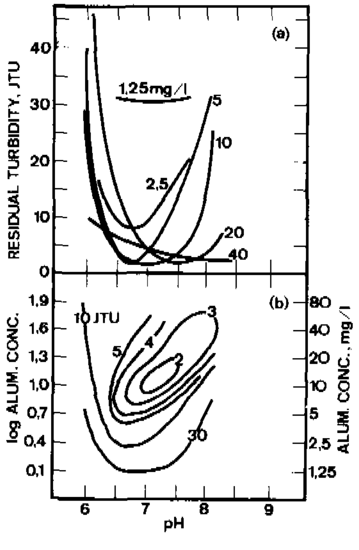

FIGURE 8.4: Example of Results for Jar Test (Settling) Experiments

8.1.6 Analysis of Results

Following the above procedure for a range of coagulant dosages and pH values, a series of curves are plotted of, for example, supernatant turbidity versus pH, each curve at a particular dosage (see Figure 8.4a). Optimisation of the results may then be conveniently carried out following a procedure used by TeKippe and Ham(19): for a given water and coagulant type, following the above procedure, there will be two independent variables: dosage and pH. Data taken from curves such as Figure 8.4a may be presented in the form of two-dimensional contour graphs as shown in Figure 8.4 b. The results shown are for supernatant turbidity after settling. However, the same method of presentation may be used for other criteria, for example membrane refiltration times.

Interpretation of results is often complex. This is especially so in the case of turbidity removal after settling. With colour the jar test procedure described above usually predicts very closely the actual in-plant performance. Returning to turbidity, the measurements are complicated by such effects as shape, size, number and refractive index of particles responsible for turbidity. For example, Black and Walters(7) showed that for equal gravimetric concentrations (± 65 mg l^{-1}) of three different clay suspensions: montmorillonite, fuller's earth and kaolinite, the respective turbidities measured were 58, 79 and 294. Specifying a global final effluent quality of, say, 5 units or less is perhaps over-stringent in the case of kaolinite, where a much higher removal efficiency would be required compared to the other two suspensions. One method of overcoming such difficulties has been to express the dosage necessary to reduce the turbidity or colour to one-half its initial value(16) but this parameter has some disadvantages for treatment plant control; the 50% dosage differs markedly from results desirable in water treatment plants. Another method is to use 90% or 95% removal as the criterion(7): A disadvantage of this is that with waters of low turbidity or colour, small changes in supernatant quality assume inordinate significance. The latter methods are perhaps more applicable to research applications. When optimising the conditions for a particular water for design purposes, reducing the effluent parameter to some fixed level is probably the most satisfactory criterion. For example, as mentioned above, reducing the turbidity to 5 units.

By repeating the procedures described in the preceeding sections for a variety of coagulants, the performance of various coagulant types may be evaluated. By comparing supernatant quality (for example) for each type a final choice as to the most appropriate coagulant to use (based on desired effluent quality, economics, availability etc.) may be made.

8.2 EVALUATING FLOCCULANT AIDS

8.2.1 General

Flocculant aids, for example polyelectrolytes, are normally added after destabilization by metal coagulants to speed up the aggregation rate or to strengthen flocs formed by metal coagulants.

Because polyelectrolytes are added in this application to enhance flocculation after destabilization is complete, it is not very meaningful to analyse, for example, supernatant quality, which is usually appropriate when evaluating primary coagulants. Packham(17) describes a procedure based on the settling velocity distribution of the suspension. The method is automated for convenience. Although more laborious, the technique may be carried out manually. When evaluating flocculant aids, the advantage in utilising a method based on settling velocity over other methods such as evaluating floc size, density, permeability, compressibility, shear strength or filtrability is that, to quote Packham(17) "coagulant (flocculant) aids are flocculants which are added to a system that is already flocculating; small differences in timing and in mixing therefore can have very large effects .... floc is very highly compressible and its properties are undoubtedly affected very considerably by any handling operation". By evaluating settling velocities, it is possible to devise a test procedure which produces flocs under carefully controlled conditions and which eliminates the necessity of any transfer operation. To lend support to Packham's suggested methodology, other researchers (5, 6, 15) point out that settling velocity determinations give by far the most meaningful results in this application.

8.2.2 Initial Choice of Flocculant Aid

At the commencement of a testing program using polymeric flocculants, it is likely that a variety of polyelectrolyte samples will be obtained from those manufacturers who can safely guarantee regular delivery in the future. Initial choices of polyelectrolyte "brands" will probably be influenced by such factors as whether the chemical is manufactured in the particular country or whether it is imported, delivery costs and so on. Having comprised a reasonable short list of "brands", there will be a range of products, each having a particular basic chemical constituent (e.g. polyacrylamide, polyamine, etc.). A useful first step in evaluating each range is to take a representative sample of each ionic group. For example, a particular range of polyelectrolyte products is divided into three groups: cationic, nonionic and anionic respectively. With information of charge density from the particular manufacturer, the cationic and anionic groups have charge densities ranging from 5 to 30% and 10 to 40% respectively. By carrying out experiments with a cationic type of charge density 30%; nonionic type of charge density 0% and anionic type of charge density 30%, an indication of the appropriate ionic group for the particular application is obtained. By further carrying out tests for the remainder of the appropriate ionic group i.e. for different molecular weights within that group, compilation of a final short list of products is possible.

8.2.3 Preparation of Polyelectrolyte Solutions

When preparing different stock solutions of flocculant aid (each of a particular type of polyelectrolyte), a method proposed by Gale (13) more readily facilitates optimisation in terms of performance and cost. All solutions should be prepared such that they are each of the same cost per unit volume. (This same procedure should also be followed when evaluating sludge conditioners). As a starting point in calculating solution strengths, the maximum recommended strength for the least expensive polyelectrolyte to be tested may be used with the strengths of the remaining polyelectrolytes calculated according to their respective costs.

When adding suitably diluted polyelectrolyte solutions (such that each successive concentration is half the previous concentration) it is recommended that constant volume fractions are added. For example, always add 50 ml to 1 litre of sample. A check should be made that the diluted solution concentrations added to samples at no time exceed those recommended by the manufacturer. For example, with many products, the highest concentration recommended before addition to samples is 0,01%.

A suitable method of preparing powder or microbead polyelectrolyte stock solutions is as follows: To a dry ± 200 ml bottle add the required quantity of polyelectrolyte followed by 3 ml of methylated spirit, methanol or ethanol, in order to wet the material. Pour on rapidly 97 ml distilled water and *immediately* agitate vigorously for 10 - 15 seconds. Continue shaking the contents of the bottle periodically for a further 30 to 60 minutes. With solid grade polyelectrolyte products the highest stock solution concentration should not be greater than 5 $g\ l^{-1}$. As described above, this concentration is appropriate for the cheapest product in the range of products to be tested. With products of higher cost, the stock solution concentration concomitantly decreases.

Volumes of stock polyelectrolyte solutions prepared as above are usually sufficient for most laboratory testing programs. However, if larger volumes are required, 500 ml or 1 l etc. of distilled water may be placed on a magnetic stirrer, say, and the required quantity of solid grade polymer added *slowly* to the vortex formed while stirring; addition of the chemical should take place over a one to two minute period. Stirring should continue, after polymer addition, at a moderate rate for one to one and a half hours.

With liquid grade polyelectrolytes, the method of preparation is simpler: The required quantity of polyelectrolyte should be added to a beaker and 90 mls of distilled water stirred in by hand to obtain a homogeneous solution.

The highest concentration stock solution should not exceed 100 g l^{-1}.

8.2.4 Experimental Procedure

The method carried out manually is as follows: After primary (metal in this case) coagulant is added (at the correct dosage and pH as determined previously) various dosages of polyelectrolyte are added during the rapid mix stage (five minutes after the primary coagulant is added(5)). The errors which may result from using beakers of small size when evaluating polyelectrolytes has been pointed out earlier (14). After a further one minute rapid mixing the stirrers are turned down to slow speed (± 50 rpm) and the sample flocculated for 15 minutes. During this time, after a period of 5 minutes slow stirring, two samples are taken at a depth of 50 mm with a bent pipette as described earlier. After the 15 minutes have elapsed the stirrers are switched off and the sample allowed to stand. Samples are then taken at the same depth of 50 mm with the bent pipette after periods of 1,0; 1,5; 2,0; 2,5; 3; 6; 9; 18 and 36 minutes settling. These samples (say 5 to 10 ml) are then, for example, auto-analysed for iron or aluminium depending on the coagulant used. Measuring the metal added as coagulant gives a direct comparative measure of the amount of floc remaining in suspension at the depth of 50 mm at the set times.

Following the above procedure, the mean settling velocity of the flocs may then be determined by standard procedures (see, for example, Camp(10)). It is assumed that after the flocculation period, flocs are sufficiently formed so that they do not increase in velocity as they settle through 50 mm, although this may not always be the case(5). By determining the effective settling velocity as above for metal coagulant only and metal coagulant plus various dosages of various polyelectrolytes, a quantitative assessment is possible of the relative merits of each combination. Furthermore, the method may be used to assess the relative merits of various chemical addition times, sequences of addition and so on.

Packham(17) suggests that since the settling velocity is related to other parameters such as floc size, density, permeability, compressibility etc. the above test has meaning for most intended purposes. This implied interrelationship between parameters has also been suggested by Gale(13).

8.3 EVALUATING SLUDGE CONDITIONERS

8.3.1 General

With sludge conditioning, the testing procedures are oriented towards evaluating two principal properties: (a) filterability of the conditioned sludge and (b) floc strength. A thorough account of the experimental techniques has been presented by Gale(13) and, therefore, the objective here is only to present a summary of the procedures.

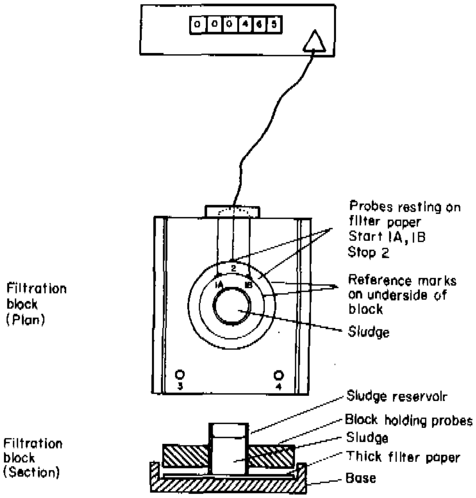

FIGURE 8.5: Capillary Suction Time Apparatus. (From Gale(13) With Permission of Uplands Press).

8.3.2 Experimental Procedures

The traditional procedure for measuring sludge filterability is to determine specific resistance. The method, described in detail elsewhere(13, 18), consists of filtering a sample of the suspension through a filter paper held in a Buchner funnel at a known constant pressure. An alternative, which has the advantage of rapidity, is the Capillary Suction Time apparatus developed by the Water Research Centre, U.K.

(3) and shown in Figure 8.5. The method relies on the suction pressure created by capillaries within absorbent paper and is, essentially, a constant pressure filtration. Whereas specific resistance is a fundamental parameter the CST is not. It can, however, be directly correlated with specific resistance for a particular bulk of sludge.

When initially preparing a short list of products to be tested, and when preparing stock conditioner solutions, identical considerations to those described for the case of flocculant aids in sections 8.2.2 and 8.2.3 are applicable here. When adding suitably diluted conditioner solutions (such that each concentration is half the previous concentration, as before) it is recommended that 20 ml of conditioner solutions of varying strengths are always added to 100 ml of sludge sample. The solutions are added to the sludge at a constant speed of stirring on a laboratory high speed stirrer (1000 rpm) during a 10 second period of mixing. After this period a portion of the sample is analysed for filterability using either specific resistance techniques or, more conveniently, the CST apparatus. The remainder of the sample is returned to the stirrer and further periods of mixing of 10, 30 and 60 seconds, applied. After each period a sample is taken and filterability determined as before. Total stirring times applied to each sample to which filterability determinations are made are 0, 10, 40 and 100 sec (excluding the initial mixing period). By determining filterability for a range of stirring periods, an indication of floc strength is achieved.

As regards initial choice of conditioners, in some cases a reliable indication is available since it is evident that the most effective conditioners are those that are also the most effective as flocculant aids; in the treatment of the same water(17).

8.4 OPTIMIZING FLOCCULATION PARAMETERS

8.4.1 General

The previous sections of this Chapter have described methods by which primary coagulant type, dosage, pH and, if used, flocculant aid are optimized for a particular water. Further tests which should be conducted on the water (but which are more often than not neglected) are those by which flocculation parameters are optimized. Up to the present time, for the design of continuous completely mixed flocculation systems, it has been necessary to obtain experimental data from continuous type pilot plant trials. Because of the considerable expenditure involved in constructing the necessary apparatus and the lengthy testing procedures involved, design of flocculation systems (especially for relatively small plants) has often been based on rule-of-thumb procedures.

For a given destabilized water, flocculation reactor geometry and agitation device, the principal parameters governing the effective degree of flocculation are the retention time and velocity gradients applied. These parameters influence the rate and extent of particle aggregation and the rate and extent of breakup of these aggregates. From an analysis of equations describing both the aggregation and breakup phases of the flocculation process, Bratby et al(8) set out the theoretical principles and experimental procedures by which it is possible to obtain design data for continuous completely mixed flocculation systems using batch test results only. The validity of the theoretical link between batch type (or plug flow) behaviour and continuous type performance was verified by comparing batch and continuous pilot scale data(8, 9) (See Section 7.2.5). The apparatus and methodology recommended by Bratby et al are presented below.

8.4.2 Apparatus

The apparatus used for evaluating flocculation performance is shown in Figure 8.6 It consists of a reactor square in plan with a capacity of 3 litres and fitted with stators. Vertical paddles are driven by a motor, the rotational speed of which is varied using a thyristor speed control. Bratby et al showed that the root mean square velocity gradient, G, in the reactor is given by the procedure of Camp(11) if k, the ratio of speed of rotation of water to speed of rotation of stirrers is taken as 0,24. Measured values of G with respect to impeller rotational speed (for the reactor shown in Figure 8.6) are shown in Figure 8.7.

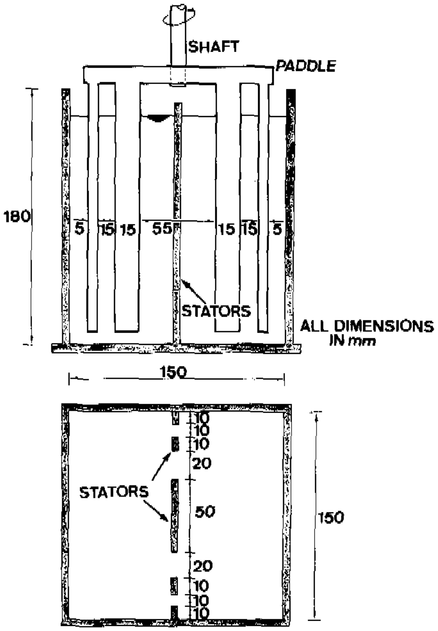

FIGURE 8.6: Reactor For Evaluating Flocculation Performance. (From Bratby et al[9]).

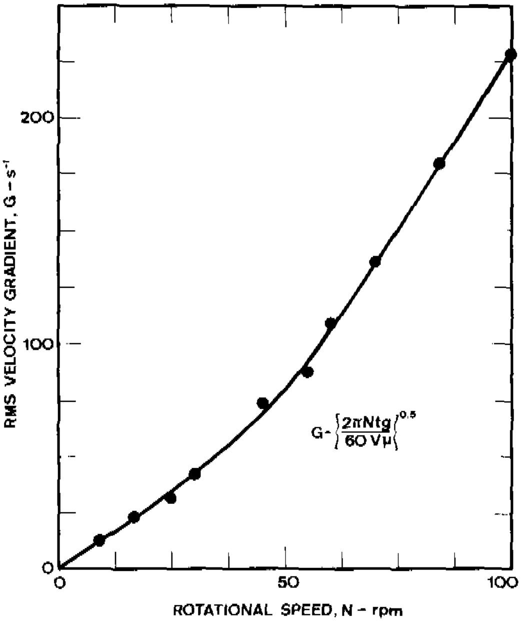

FIGURE 8.7: G Values Produced For a Range of Impeller *Rotational Speeds for Reactor Shown in Figure* 8.6 (From Bratby et al[9]).

8.4.3 Experimental Procedure

The experimental procedure is as follows: The reactor is filled to the 3 l mark with the raw water to be tested. The stirrer is set to the maximum rotational speed (preferably 300 rpm) giving a G value of approximately 1000 $\sec^{-1}$. Immersing a pH probe in the reactor contents, the pH is adjusted to the initial value found optimal previously and the correct primary coagulant type and dosage (previously determined) are added (see Section 8.1). After say 5 minutes rapid mixing, flocculant aid, if required, is added. Note that all chemicals used, their dosages, sequence of addition, time lag between dosing, etc., follow exactly those found optimal in the experiments described previously.

After, say, a further 1 minute rapid mixing the stirrers are slowed down to the speed corresponding to the G value set for that particular experiment and stirring is continued for the time also set for that test. After the given time has elapsed stirring is stopped and in cases where settling is the criterion of interest, the flocs allowed to settle for a given time, say 30 minutes. The settling time should correspond to a time slightly greater than that beyond which no significant improvement in supernatant quality is evident. (Note that previous comments concerning the criteria describing process performance, Section 8.1.4, are also applicable here).

A sample is then withdrawn at a depth of 30 mm from the surface (using the bent pipette described earlier) and analysed for some parameter representative of the number of primary particles which remain unflocculated (and, therefore, are present in the supernatant sample). The actual parameter used depends on the type of water under test. For example, for a turbid water the appropriate parameter is turbidity. For a coloured water UV spectrophotometric measurements are probably the most appropriate. For a water destabilized with a metal (primary) coagulant and subsequently with a coagulant aid (e.g. a polyelectrolyte) analysing for the metal (aluminium or iron) will probably give the most meaningful results.

For a range of G values and flocculation periods, a series of curves of best fit are drawn through plotted values of N_o/N versus flocculation period, T (as shown in Figures 8.8a (8) and b(9)). Note that N_o = initial supernatant turbidity (or colour or metal concentration etc.) after destabilization and after settling, *but at zero flocculation period,* and N = supernatant turbidity (etc.) after a flocculation period, T, and after settling.

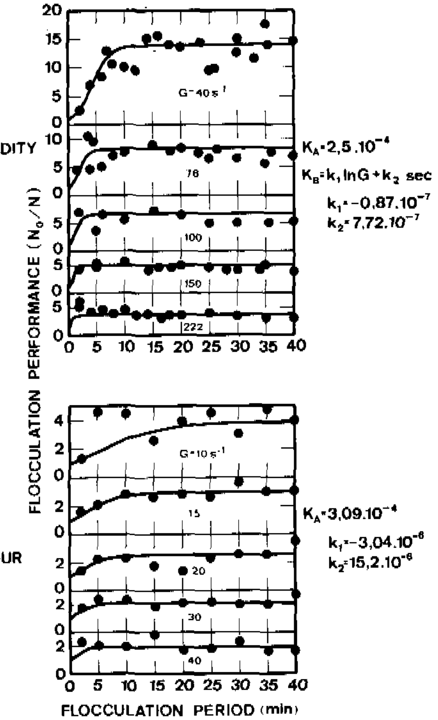

FIGURE 8.8: Flocculation Performance, No/N, for a Range of Flocculation Times and G Values for (a) Turbid and (b) Coloured Water. (Adapted from Bratby et al(8, 9)).

From curves such as those shown in Figures 8.8a and b, the flocculation and breakup constants, K_A and K_B are determined by fitting Equation 7.25 to the curves. Assuming that the number concentration of primary particles, n, is proportional to supernatant turbidity (etc.), N, equations 7.23 and 7.25 may thus be rewritten as

$$\frac{N_o}{N_m} = \frac{(1+K_A\ GT/m)^m}{1+K_B\ G^2\ T/m \sum_{i=0}^{m-1} (1+K_A\ GT/m)^i} \qquad (8.1)$$

for a continuous, completely mixed in-series system of flocculation reactors and

$$\frac{N_o}{N} = \left[\frac{K_B}{K_A} G + \left(1 - \frac{K_B}{K_A} G\right) e^{-K_A GT}\right]^{-1} \qquad (8.2)$$

for a batch or plug flow system

where N_o and N are as given above;

N_m = supernatant turbidity of m - th reactor in series of completely mixed flow through reactors with total retention time in m reactors, T;

K_A = flocculation constant;

K_B = breakup constant;

G = root mean square velocity gradient.

8.4.4 Analysis of Data

Bratby et al demonstrated the inadequacy of the assumed break-up mechanism giving rise to an over-prediction of floc erosion at high G values. This is reflected in the fact that when fitting Equations 8.1 and 8.2 to experimental data, K_B does not remain constant for each G value applied. In terms of interpreting the laboratory data for design, however, this does not present a problem since the same variation in K_B is evident during continuous operation. In the light of the foregoing, the following methodology is recommended when determining the values of K_A and K_B from experimental data (analysis is greatly facilitated by the use of programmable "hand-held" or "desk-top" calculators):

(i) From the horizontal portion of the curves (the experiments should be conducted such that a significant horizontal portion is produced) the ratio K_B/K_A is determined from

$$K_B/K_A = 1/(G.N_o/N) \qquad (8.3)$$

(ii) Taking successive points on the curves of best fit for each G value, values of K_A are determined from a re-arrangement of Equation (8.2), i.e.

$$K_A = \frac{1}{GT} \ln \left\{ \frac{(1 - \frac{K_B}{K_A} . G)}{(\frac{1}{N_o/N} - \frac{K_B}{K_A} G)} \right\} \qquad (8.4)$$

(iii) From the K_A values calculated for each point on the curve for each particular G value, the mean value is calculated and, from the values of K_A/K_B for each curve, the values of K_B for each curve are calculated.

(iv) Plot the values of K_B as ordinate and ln G as abscissa. The value of K_B at any G value is given by a relationship of the form

$$K_B = k_1 \ln G + k_2 \qquad (8.5)$$

where k_1 and k_2 are constants for a particular water.

For Figure 8.8a, which shows a re-analysis of the results of Bratby et al for a kaolin clay suspension using aluminium sulphate as coagulant(8), K_B is given by

$$K_B = (7{,}72 - 0{,}87 \ln G)\ 10^{-7} \text{ sec.}$$

For Figure 8.8b, which shows results for a water with zero initial turbidity but coloured with humic substances and using aluminium sulphate as coagulant(9), K_B is given by

$K_B = (15{,}2 - 3{,}04 \ln G)\, 10^{-6}$ sec.

For the turbid (kaolin clay) suspension, K_A was found to be $2{,}5.10^{-4}$ and for the coloured water $K_A = 3{,}09.10^{-4}$.

(v) From the values of K_A and K_B determined as above, the curves are replotted and, if necessary, the values of K_A and/or K_B adjusted slightly to give the best fit to all the curves at each G value. Note that the K_A value is constant throughout the G values but K_B may vary with G as demonstrated above.

It should be noted that the empirical relationship between the breakup constant, K_B and velocity gradient, G, given above is for convenience in analysis. The need for such a relationship further illustrates the inadequacy of the breakup mechanism assumed, as mentioned earlier. For design purposes, however, this inadequacy is unimportant since the results from batch tests may be applied directly (taking cognisance of the different formulations pertaining) to continuous completely mixed systems(8, 9).

Having determined the constants K_A and K_B, the design of a flocculation system for the particular (destabilized) water under test may be made following the procedures described earlier. As stated previously, during the coagulation testing stage a number of chemical combination alternatives will probably be available. These may now be finally optimised, having assessed the optimal flocculation performance of each combination. A final comparative economic assessment is carried out where running (chemical) costs are weighed against capital (flocculation) costs.

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A.1 PERIODIC TABLE OF THE ELEMENTS

(From R. C. West(ed.), *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, Ohio, 1964(45th ed.), with permission of the publisher).

1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0	Orbit
1 +1 -1 H 1.00797 1					Atomic Number → **50** +2 +4 ← Oxidation States KEY TO CHART Symbol → Sn Atomic Weight → 118.69 -18-18-4 ← Electron Configuration												**2** 0 He 4.0026 2	K
3 +1 Li 6.939 2-1	**4** +2 Be 9.0122 2-2											**5** +3 B 10.811 2-3	**6** +2 +4 -4 C 12.01115 2-4	**7** +1 +2 +3 +4 +5 -1 -2 -3 N 14.0067 2-5	**8** -2 O 15.9994 2-6	**9** -1 F 18.9984 2-7	**10** 0 Ne 20.183 2-8	K-L
11 +1 Na 22.9898 2-8-1	**11** +2 Mg 24.312 2-8-2				Transition Elements			Group 8		Transition Elements		**13** +3 Al 26.9815 2-8-3	**14** +2 +4 -4 Si 28.086 2-8-4	**15** +3 +5 -3 P 30.9738 2-8-5	**16** +4 +6 -2 S 32.064 2-8-6	**17** +1 +5 +7 -1 Cl 35.453 2-8-7	**18** 0 Ar 39.948 2-8-8	K-L-M
19 +1 K 39.102 -8-8-1	**20** +2 Ca 40.08 -8-8-2	**21** +3 Sc 44.956 -8-9-2	**22** +2 +3 +4 Ti 47.90 -8-10-2	**23** +2 +3 +4 +5 V 50.942 -8-11-2	**24** +2 +3 +6 Cr 51.996 -8-13-1	**25** +2 +3 +4 +7 Mn 54.9380 -8-13-2	**26** +2 +3 Fe 55.847 -8-14-2	**27** +2 +3 Co 58.9332 -8-15-2	**28** +2 +3 Ni 58.71 -8-16-2	**29** +1 +2 Cu 63.54 -8-18-1	**30** +2 Zn 65.37 -8-18-2	**31** +3 Ga 69.72 -8-18-3	**32** +2 +4 Ge 72.59 -8-18-4	**33** +3 +5 -3 As 74.9216 -8-18-5	**34** +4 +6 -2 Se 78.96 -8-18-6	**35** +1 +5 -1 Br 79.909 -8-18-7	**36** 0 Kr 83.80 -8-18-8	-L-M-N
37 +1 Rb 85.47 -18-8-1	**38** +2 Sr 87.62 -18-8-2	**39** +3 Y 88.905 -18-9-2	**40** +4 Zr 91.22 -18-10-2	**41** +3 +5 Nb 92.906 -18-12-1	**42** +6 Mo 95.94 -18-13-1	**43** +4 +6 +7 Tc (99) -18-13-2	**44** +3 Ru 101.07 -18-15-1	**45** +3 Rh 102.905 -18-16-1	**46** +2 +4 Pd 106.4 -18-18-0	**47** +1 Ag 107.870 -18-18-1	**48** +3 Cd 112.40 -18-18-2	**49** +3 In 114.82 -18-18-3	**50** +2 +4 Sn 118.69 -18-18-4	**51** +3 +5 -3 Sb 121.75 -18-18-5	**52** +4 +6 -2 Te 127.60 -18-18-6	**53** +1 +5 +7 -1 I 126.9044 -18-18-7	**54** 0 Xe 131.30 -18-18-8	-M-N-O
55 +1 Cs 132.905 -18-8-1	**56** +2 Ba 137.34 -18-8-2	**57*** +3 La 138.91 -18-9-2	**72** +4 Hf 178.49 -32-10-2	**73** +5 Ta 180.948 -32-11-2	**74** +6 W 183.85 -32-12-2	**75** +4 +6 +7 Re 186.2 -32-13-2	**76** +3 +4 Os 190.2 -32-14-2	**77** +3 +4 Ir 192.2 -32-15-2	**78** +2 +4 Pt 195.09 -32-16-2	**79** +1 +3 Au 196.967 -32-18-1	**80** +1 +2 Hg 200.59 -32-18-2	**81** +1 +3 Tl 204.37 -32-18-3	**82** +2 +4 Pb 207.19 -32-18-4	**83** +3 +5 Bi 208.980 -32-18-5	**84** +2 +4 Po (210) -32-18-6	**85** At (210) -32-18-7	**86** 0 Rn (222) -32-18-8	-N-O-P
87 +1 Fr (223) -18-8-1	**88** +2 Ra (227) -18-8-2	**89**** +3 Ac (227) -18-9-2																-O-P-Q

*Lanthanides	58 +3 +4 Ce 140.12 -19-9-2	59 +3 Pr 140.907 -20-9-2	60 +3 Nd 144.24 -22-8-2	61 +3 Pm (145) -23-8-2	62 +2 +3 Sm 150.35 -24-8-2	63 +2 +3 Eu 151.96 -25-8-2	64 +3 Gd 157.25 -25-9-2	65 +3 Tb 158.924 -26-9-2	66 +3 Dy 162.50 -28-8-2	67 +3 Ho 164.930 -29-8-2	68 +3 Er 167.26 -30-8-2	69 +3 Tm 168.934 -31-8-2	70 +2 +3 Yb 173.04 -32-8-2	71 +3 Lu 174.97 -32-9-2	-N-O-P
**Actinides	**90** +4 Th 232.038 -19-9-2	**91** +5 +4 Pa (231) -20-9-2	**92** +3 +4 +5 +6 U 238.03 -21-9-2	**93** +3 +4 +5 +6 Np (237) -22-9-2	**94** +3 +4 +5 +6 Pu (242) -23-9-2	**95** +3 +4 +5 +6 Am (243) -24-9-2	**96** +3 Cm (245) -25-9-2	**97** +3 +4 Bk (249) -26-9-2	**98** +3 Cf (249) -28-8-2	**99** Es (254) -29-8-2	**100** Fm (252) -30-8-2	**101** Md (256) -31-8-2	**102** (254) -32-8-2	**103** Lw	-O-P-Q

Numbers in parentheses are mass numbers of most stable isotope of that element.

A.2 POLYELECTROLYTES ACCEPTABLE FOR USE IN POTABLE WATER TREATMENT

The following tables present the current lists (at the time of writing) of polyelectrolytes acceptable for use in potable water treatment supplied by the Department of the Environment, U.K., and the Environmental Protection Agency, U.S.A. respectively.

The lists, as presented here, have been arranged in alphabetical order of product names. Certain supplementary information has been included where possible. In cases where the information is not available at the time of writing, the corresponding entry is left blank.

Although much of the information required to complete the lists was not available and furthermore, the lists of approved products are periodically updated by the above agencies, it was felt worthwhile to include such a list not only as a convenient reference source but also to enable information to be updated or entered as appropriate at a later stage.

It should also be noted that the products listed do not comprise the whole range of polyelectrolytes available. There are many products which, although not cleared for use in potable water treatment, are widely used successfully in numerous wastewater and industrial applications. However, to include all polyelectrolytes available is impracticable in a book of this nature.

A.2.1 List of Approved Products Supplied by the Department of the Environment, U.K.

The following list essentially reproduces the Section "Coagulants and Coagulant Aids" from the Tenth Statement (May 1977) issued by the "Committee on New Chemicals and Materials of Construction for Use in Public Water Supply and Swimming Pools" of the Department of the Environment, 2 Marsham Street, London SW1P 3EB, England, U.K.

For products based on polyacrylamide, or acrylamide/acrylate copolymers, the following conditions apply: No batch may contain more than 0,05% free acrylamide monomer based on the active polymer content; An upper limit for the content of free acrylamide monomer must be stated by the supplier for every batch; The method of analysis for free acrylamide monomer is that described by the Water Research Association Technical Inquiry Report nº 171 (Water Research Centre, P.O. Box 16, Henley Rd., Medmenham, Marlow SL7 2HD, England, U.K.) with the exception of the PURIFLOC products, where the method of analysis to be used is that published in "Analytical Chemistry", 37, Nov., p. 1546, 1965.

For products based on polyacrylic acid, no batch may contain more than 0,5% of free acrylic acid monomer based on the active polymer content.

Note that where polyelectrolyte type is entered, the following abbreviations signifying the basis of the product, are used: PAC (polyacrylamide or acrylamide/acrylate copolymer); PA (polyacrylic acid); SA (sodium alginate); PDADMAC (polydiallyldimethylammonium chloride); PAD (polyamide); PAM (polyamine); ALUM (aluminium); PQR (polyquaternary resin); PEI (polyethylenimine).

The letter after the polyelectrolyte type entry: (s) or (l) indicates whether the product is of solid (powder, micro-bead etc.) grade or liquid grade.

Cationic; nonionic or anionic charge types are designated (+); (0) or (-) and occur before the degree of ionization or charge density entry.

						MAX. DOSAGE		
	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	AVE. mg/l	MAX. mg/l	COMMENTS
01	AQUAFLOC 4171	Dearborn Chem. Ltd., Foundry Lane, Ditton, Widnes, Cheshire, WA8 8TZ	PAC			0,5	1,0	
02	AQUAFLOC 4174		PAC			0,5	1,0	
03	AQUAFLOC 4270		PAC			0,5	1,0	
04	BETZ POLYMER 1190	Betz Ltd., Nat. Lane, Winsford, Cheshire CW7 385	PQR			-	10,0	
05	BETZ POLYMER 1290		PQR			-	10,0	
06	BUFLOC 30	Buckman Lab. SA, Wondelgemkaai 157, B-9000 Ghent, Belgium	PA			-	10,0	
07	CATFLOC	Chemviron, Div. of Baltimore, Chausee de Waterloo, 1135 1180 - Bruxelles	PDADMAC (1)	(+)		-	7,0	
08	DECAPOL A11P	Fospur Ltd., Alfreton Ind. Est., Nottingham Rd., Somercotes, Derby, DE5 4LR	PAC			0,5	1,0	
09	DECAPOL A30P		PAC(s)	(-)<10%	-15.10^6	0,5	1,0	
10	DECAPOL A33P		PAC(s)	10- (-) 20%	-15.10^6	0,5	1,0	
11	DECAPOL A39P		PAC(s)	(-) 30-40%	-15.10^6	0,5	1,0	
12	DECAPOL A45P		PAC(s)	(-) 50-60%	-15.10^6	0,5	1,0	
13	DECAPOL C300P		PAC	(+)		0,5	1,0	
14	DECAPOL C330P		PAC(s)	(+) 15-25%	-5.10^6	0,5	1,0	
15	DECAPOL N11P		PAC	(0)		0,5	1,0	
16	DECAPOL N100P		PAC(s)	(0) -2%	-15.10^6	0,5	1,0	
17	DECAPOL N50P		PAC(s)	(0)	-15.10^6	0,5	1,0	
18	DECAPOL N10P		PAC	(0)		0,5	1,0	
19	DECAPOL C11P		PAC	(+)		0,5	1,0	
20	DECAPOL C10P		PAC	(+)		0,5	1,0	
21	DECAPOL C100P		PAD(1)	(+)	$> 10^6$	-	10,0	
22	DECAPOL C101P		PQR(1)	(+)	$> 10^6$	-	10,0	
23	DECAPOL C102P		PQR	(+)		-	10,0	
24	FLOCBEL F2	Float Ore Ltd., Apex. Wks., Willow Bank, Uxbridge, Middlesex, UB9 4AF	PAC			0,5	1,0	
25	FLOCBEL F3		PAC			0,5	1,0	
26	FLOCBEL F4		PAC			0,5	1,0	
27	FLOCCOTAN A (35% active content)	Dearborn Chem Ltd., Foundry Lane, Ditton, Widnes, Cheshire, WA8 8TZ	Tannin (1)			-	10,0	
28	FLOCGEL E30	Royal Scholten Honig (Trading Ltd.), Moss Lane, Whitefield, Manchester, M25 6FM	Starch			-	5	
29	FOSTARCH 4P	Fospur Ltd., Alfreton Ind. Est., Somercotes, Derby, DE5 4LR	Starch			-	3	
30	FOSTARCH 5P		Starch			-	3	
31	FOSTARCH 6P		Starch			-	3	
32	HERCOFLOC 812	Hercules Powder Co. Ltd., 1 Gt. Cumberland Place, London W1H 8AL	PAC			0,5	1,0	
33	HERCOFLOC 815		PAC			0,5	1,0	
34	HERCOFLOC 818		PAC			0,5	1,0	
35	HERCOFLOC 821		PAC			0,5	1,0	
36	HERCOFLOC 839		PAC			0,5	1,0	
37	MAGNAFLOC LT20	Allied Colloids Mnfg. Co. Ltd., Low Moor, Bradford, Yorks., BD12 0JZ	PAC(s)	(0) 0%	$> 7.10^6$	0,5	1,0	
38	MAGNAFLOC LT21		PAC			0,5	1,0	
39	MAGNAFLOC LT22		PAC(s)	(+) 30%	$> 7.10^6$	0,5	1,0	
40	MAGNAFLOC LT22S		PAC			0,5	1,0	
41	MAGNAFLOC LT24		PAC(s)	(+) 10%	$> 7.10^6$	0,5	1,0	
42	MAGNAFLOC LT25		PAC(s)	(-) 30%	$> 7.10^6$	0,5	1,0	
43	MAGNAFLOC LT26		PAC(s)	(-) 40%	$> 7.10^6$	0,5	1,0	
44	MAGNAFLOC LT27		PAC			0,5	1,0	
45	MAGNAFLOC LTD28		PAC			0,5	1,0	
46	MAGNAFLOC LT29		PAC			0,5	1,0	
47	NALFLOC A373	Nalfloc Ltd., PO Box 11, Mond House, Winnington, Northwich, Cheshire CW8 4DX	PAC			0,5	1,0	
48	NALFLOC A378		PAC			0,5	1,0	
49	NALFLOC N8170		PAC			0,5	1,0	
50	NALFLOC N607		PAM			-	7,0	
51	OAKITE CLARIFIER SF 3	Oakite Ltd., West Carr Rd., Ind. Estate, Rettford, Notts, DN22 7SN	PA			-	10	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE AVE. mg/l	MAX. DOSAGE MAX. mg/l	COMMENTS
52	PAC	Alumina Co. Ltd., Ditton Rd. Wks., Widnes, Cheshire WA8 OPH	ALUM			-	200	
53	PAC	Laporte Ind. Ltd., Acids and Aluminas, Moorfield Rd., Widnes, Cheshire WA8 OHE	ALUM			-	200	
54	PERFECTAMYL AS 114/3	Tunnel Avebe Starches Ltd., Avebe House, Otterham Quay, Rainham, Gillingham, Kent ME8 7UU	Starch	(+)	$> 10^6$	-	3	
55	PERFECTAMYL AS 114/2		Starch	(0)	$> 10^6$	-	5	
56	PERFECTAMYL AS 114/2 (without boron)		Starch	(0)	$> 10^6$	-	5	
57	POLYMER 233	Chemviron, Div. of Baltimore, Aircoil-Chemviron SA Chausee de Waterloo 1135, 1180 Bruxelles	PAC			0,5	1,0	
58	POLYMER 243		PAC			0,5	1,0	
59	POLYMER 253		PAC			0,5	1,0	
60	PURIFLOC N127	Ash Spinning Co. Ltd., Chem. Div., Jubilee St., Shaw, Near Oldham OL2 8PL	PAC			0,5	1,0	
61	PURIFLOC N17		PAC			0,5	1,0	
62	PURIFLOC A22		PAC			0,5	1,0	
63	PURIFLOC A23		PAC			0,5	1,0	
64	PURIFLOC A24		PAC			0,5	1,0	
65	SANPOLY 305 (PWG)	Chem. Dept. Mitsubishi Corp., Bow Bells Hse., Broad St., Cheapside, London EC4M 9BQ	PAC			0,5	1,0	
66	SANPOLY A510 (PWG)		PAC			0,5	1,0	
67	SANPOLY A520 (PWG)		PAC			0,5	1,0	
68	SANPOLY N500 (PWG)		PAC			0,5	1,0	
69	STADEX WTA	Starch Products Ltd., Stadex Wks., Middle Green Rd., Langley, Slough SL3 6BX	Starch			-	3,0	
70	STADEX WTB		Starch			-	3,0	
71	STADEX WTC		Starch			-	3,0	
72	STADEX WS612		Starch			-	5,0	
73	SUPERFLOC A100 (PWG)	Cyanamid of Gb., Ind. Products Div., Fareham Rd., Gosport, PO Box 7, Hants, PO13 OAS	PAC(s)	(-)		0,5	1,0	
74	SUPERFLOC A110 (PWG)		PAC(s)	(-)	-15.10^6	0,5	1,0	
75	SUPERFLOC A130 (PWG)		PAC(s)	(-)		0,5	1,0	
76	SUPERFLOC A150 (PWG)		PAC(s)	(-)		0,5	1,0	
77	SUPERFLOC C100 (PWG)		PAC(s)	(+)		0,5	1,0	
78	SUPERFLOC C110 (PWG)		PAC(s)	(+)		0,5	1,0	
79	SUPERFLOC N100 (PWG)		PAC(s)	(0)	-15.10^6	0,5	1,0	
80	SUPERFLOC 992		PAC			0,5	1,0	
81	SUPERFLOC 521		PAD(1)	(+)		-	10,0	
82	SUPERFLOC 573		PQR(1)	(+)	$- 5.10^4$	-	10,0	
83	SUPERFLOC 577		PQR (1)	(+)	high	-	10,0	
84	TAPA	Buckman Lab. SA, Wondelgemkaai 157, B-9000 Ghent, Belgium	PA			-	10,0	
85	TRW 90AP	TR Int. (Chem.) Ltd., Cheadle Heath, Stockport, Cheshire SK3 ORY	PAC			0,5	1,0	
86	TRW 91AP		PAC			0,5	1,0	
87	TRW 93AP		PAC			0,5	1,0	
88	TRW 95AP		PAC			0,5	1,0	
89	TRW 90CP		PAC			0,5	1,0	
90	TRW 91CP		PAC			0,5	1,0	
91	TRW 80NP		PAC			0,5	1,0	
92	WELGUM S	Alginate Ind. Ltd., 22 Henrietta St., London WC2E 8NB	SA			-	1,0	
93	WISPROFLOC-P	WA Scholten's Fabrieken NV, Foxhol, Postbus 1, Holland	Starch			-	3,0	
94	WISPROFLOC-20		Starch			-	5,0	

A.2.2 List of Approved Products Supplied by the Environmental Protection Agency, U.S.A.

The following list essentially reproduces the "Report on Coagulant Aids for Water Treatment" (August 1978) issued by the Technical Support Division, Office of Drinking Water, Office of Water and Waste Management, 5555 Ridge Rd., Cincinnati, Ohio 45268 of the United States Environmental Protection Agency.

The original report points out that the maximum recommended concentrations given are confined to their use in drinking water plants. Some of the products listed may kill fish at or below maximum recommended concentrations. Users should obtain information on fish toxicity, biointensification and biodegradability from the manufacturers if required.

Abbreviations used below are identical to those used in Section A.2.1.

Note that for DREWFLOC 1 the recommended dosage is 1 part Drewfloc to 8 parts alum when used simply as an aid in alum coagulation, and 0,5 mg/1 Drewfloc to 10 mg/1 lime when used with lime softening.

						MAX. DOSAGE		
	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	AVE. mg/1	MAX. mg/1	COMMENTS
01	ACTASOL	PQ Systems, Inc., P.O. Box 842 Valley Forge, PA					10,0	
02	ALCO-FLOC 8	Aqua Lab. and Chem. Co.Inc. P.O. Box 5725, Longview, Texas 75604					20,0	
03	ALLSTATE Nº 2	Allstate Chem. Co., Box. 3040, Euclid, OH 44117					3,0	
04	ALLSTATE Nº 6						1,0	
05	AMERFLOC 2	Drew Chem. Corp., 701 Jefferson Rd., Parsippany, NJ 07054					10,0	
06	AMERFLOC 10		(1)				50,0	
07	AMERFLOC 265		(s)				1,0	
08	AMERFLOC 275		(s)				1,0	
09	AMERFLOC 307		(s)				1,0	
10	AMERFLOC 420						10,0	
11	AMERFLOC 435		(1)				30,0	
12	AMERFLOC 440		(1)				30,0	
13	AMERFLOC 445		(1)				30,0	
14	AMERFLOC 485		(1)				20,0	
15	AMERFLOC 490		(1)				20,0	
16	AMERFLOC 2265		(1)	(-)			4,0	
17	AQUAFLOC 401	Dearborn Chem (US), 300 Genesee St., Lake Zurich, IL 60047					50,0	
18	AQUAFLOC 408		(1)				50,0	
19	AQUAFLOC 409						1,0	
20	AQUAFLOC 411						30,0	
21	BAYFLOC 901	Bay Chem and Supply Co., PO Box 1581, Corpus Christi, Texas 78403					50,0	
22	BERDELL N-489	Berdell Ind., 8-16 43rd Ave., Long Island City, NY 11101					1,0	
23	BERDELL N-821						1,0	
24	BERDELL N-902						1,0	
25	BETZ Polymer 1100P	Betz Lab., Inc., Somerton Rd., Trevose, PA 19047					1,0	
26	BETZ Polymer 1110P						1,0	
27	BETZ Polymer 1120P			(-) 15-30%	-5.10^6		1,0	
28	BETZ Polymer 1130P						1,0	
29	BETZ Polymer 1140P						1,0	
30	BETZ Polymer 1150P						1,0	
31	BETZ Polymer 1160P						1,0	
32	BETZ Polymer 1190		PQR				20,0	
33	BETZ Polymer 1200P						1,0	
34	BETZ Polymer 1205P						1,0	
35	BETZ Polymer 1210P						1,0	
36	BETZ Polymer 1220P						1,0	
37	BETZ Polymer 1230P						1,0	
38	BETZ Polymer 1240P						1,0	
39	BETZ Polymer 1250P						1,0	
40	BETZ Polymer 1260P						1,0	
41	BETZ Polymer 1290		PQR				20,0	
42	BETZ Polymer 2800P						1,0	
43	BETZ Polymer 2810P						1,0	
44	BETZ Polymer 2820P						1,0	
45	BETZ Polymer 2830P						1,0	
46	BETZ Polymer 2840P						1,0	
47	BETZ Polymer 2850P						1,0	
48	BETZ Polymer 2860P						1,0	
49	BETZ Polymer 2890P						20,0	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE AVE. mg/l	MAX. mg/l	COMMENTS
50	BETZ Polymer 3300P						1,0	
51	BETZ Polymer 3310P						1,0	
52	BETZ Polymer 3320P						1,0	
53	BETZ Polymer 3330P						1,0	
54	BETZ Polymer 3340P						1,0	
55	BETZ Polymer 3350P						1,0	
56	BETZ Polymer 3360P						1,0	
57	BETZ Polymer 3390P						20,0	
58	BETZ Polymer 1115LP						4,0	
59	BETZ Polymer 1215LP						4,0	
60	BETZ Polymer 2815LP						4,0	
61	BETZ Polymer 3315LP						4,0	
62	BETZ Entec 600						30,0	
63	BETZ Entec 610						20,0	
64	BETZ Entec 620						1,0	
65	BETZ Entec 622						1,0	
66	BONDFLOC Nº 1-101	Bond Chem. Inc., 1500 Brook Park Rd., Cleveland, OH. 44109					5,0	
67	BRENCO 870	Brennan Chem. Co., 704 North 1st. St., St. Louis, MO 63102					100,0	
68	BRENCO 880						100,0	
69	BURTONITE 78	The Burtonite Co., Nutley, NJ 07110					5,0	
70	CARBOXYMETHYLCELLULOSE	Hercules Inc., 910 Market St., Wilnington, DE 19899					1,0	
71	CAT-FLOC	Calgon Corp. P.O. Box 1346 Pittsburgh, PA 15222	PDADMAC (1)	(+)			7,0	
72	CAT-FLOC A						80,0	
73	CAT-FLOC B		PDADMAC (1)	(+)	$<10^6$		10,0	
74	CAT-FLOC C						25,0	
75	CAT-FLOC S						33,3	
76	CAT-FLOC T		PDADMAC (1)	(+)			50,0	
77	CAT-FLOC T-1		(1)	(+)			5,0	
78	CAT-FLOC 21						15,0	
79	CAT-FLOC 121						6,0	
80	COAGULANT AID 2						1,0	
81	COAGULANT AID 18						15,0	
82	COAGULANT AID 233		(s)	(0)			1,0	
83	COAGULANT AID 243		(s)	(-) High	High		1,0	
84	COAGULANT AID 253		(s)	(-) med.	High		1,0	
85	COAGULANT AID 961						5,0	
86	COAGULANT AID 72A	Garrett-Callahan, 111 Rollins Rd., Millbrae, CA 94031					50,0	
87	COAGULANT AID 74B						30,0	
88	COAGULANT AID 76						40,0	
89	COAGULANT AID 76A						50,0	
90	COAGULANT AID 78B						50,0	
91	COPOLYMER GR-989	W.R. Grace and Co., Research Div., 7379 Route 32,, Columbus, MD 21044					1,0	
92	COPOLYMER GR-996						1,0	
93	COPOLYMER GR-997						1,0	
94	CYFLOC (R) 4500	American Cyanamid Co., Berdan Ave., Wayne, NJ 07470					1,0	
95	CYFLOC (R) 5500						4,0	
96	CYFLOC (R) 6000						10,0	
97	DOWELL M-143	Dow Chemical USA, Barstow Bldg., 2020 Dow Centre, Midland, MI 48640					5,0	
98	DREWFLOC 1	Drew Chem.Corp., 701 Jefferson Rd., Parsippany, NJ 07054	(1)					
99	DREWFLOC 3						3,0	
100	DREWFLOC 4						5,0	
101	DREWFLOC 21		(1)	(+)			5,0	
102	DREWFLOC 922						10,0	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE		COMMENTS
						AVE. mg/l	MAX. mg/l	
103	F-86	Culligan, USA, One Culligan Pkwy, Northbrook, IL 60062					180,0	
104	FABCON	Fabcon Int., 1275 Columbus Ave., San Francisco, CA 94133					0,5	
105	FLOC-AID 1038	National Starch and Chem. Corp., 1700 W Front St., Plainfield, NJ 07063					5,0	
106	FLOC-AID 1063						5,0	
107	FLOCCULITE 550	DuBois Chem., Div. of WR Grace and Co., 3630 E. Kemper Rd., Sharonville, OH 45241					2,0	
108	FLOCCULITE 551						1,0	
109	FLOCGEL	KSH Chemicals Corp., 311 Cox St., Roselle, NJ 07203					10,0	
110	FO-107	W.R. Grace and Co., Research Div., 7379 Route 32, Columbus, MD 21044					1,0	
111	FO-115						1,0	
112	FORMULA 70A	Garrett-Callahan, 111 Rollins Rd., Milbrae, CA 94031					50,0	
113	FORMULA 73						50,0	
114	FORMULA 74E						20,0	
115	GAMAFLOC NI 702	Gamlen Chem., Co., 4 Midland Ave., Elmwood, NJ 07407					4,0	
116	GAMAFLOC PWS						5,0	
117	GAMLEN WIS-PROFLOC 20						5,0	
118	GAMLOSE W						5,0	
119	GOTHOFLOC 283 PWG	Gotham Chem. Co., 27 Traverse Ave., PO Box 133, Port Chester NY 10573					10,0	
120	GOTHOFLOC 383 PWG						5,0	
121	GR-962	W.R. Grace & Co., Research Div., 7379 Route 32, Columbus MD 21044					1,0	
122	GR-963						1,0	
123	GUARTEC F	General Mills Chem., 4620 W. 77th St., Minneapolis, MN 55435					10,0	
124	GUARTEC SJ						10,0	
125	GWP-16A-LT	DuBois Chem., Div. of W.R. Grace and Co., 3630 E Kemper Rd., Sharonville, OH 45241					4,0	
126	HALLMARK 81	Celanese Polymer Specialities Co., P.O. Box 99038, Jeffersontown, KY 40299					1,0	
127	HALLMARK 82						1,0	
128	HAMACO 196	A.E. Staley Mfg. Co., P.O. Box 151, Decatur, IL 62525					5,0	
129	HERCOFLOC 805 PWG	Hercules Inc., 910 Mkt. St., Wilmington, DE 19899					1,0	
130	HERCOFLOC 812 PWG		PAC				1,0	
131	HERCOFLOC 815 PWG		PAC				1,0	
132	HERCOFLOC 818 PWG		PAC				1,0	
133	HERCOFLOC 871 PWG		PAC				1,0	
134	HERCOFLOC 863						5,0	
135	HERCOFLOC 1018 PWG						1,0	
136	HERCOFLOC 1021 PWG						1,0	
137	HERCOFLOC 1031 PWG						1,0	
138	HERCULES SP944						0,05	
139	HOMOPOLYMER GR-999	W.R. Grace & Co., Research Div., 7379 Route 32, Columbus, MD 21044					1,0	
140	ILLCO IFA 313	Illinois Wat. Treat. Co., 840 Cedar St., Rockford, IL 61102					10,0	
141	JAGUAR	Celanese Polymer Specialities Co., P.O. Box 99038 Jeffersontown KY 40299					0,5	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE AVE. mg/l	MAX. mg/l	COMMENTS
142	KELGIN W	Kelco Co., 8225 Aero Drive, San Diego, CA 92123					2,0	
143	KELCOSOL						2,0	
144	KORIFLOC PA-322	Kurita Water Ind., c/o C. ITOH & Co., (America) Inc., 270 Park Ave., New York, NY 10017					1,0	
145	KORIFLOC PA-331						1,0	
146	L-650E	Calgon Corp., P.O. Box 1346 Pittsburgh, PA 15222					4,0	
147	L-675						1,0	
148	MAGNIFLOC 513C	American Cyanamid Co., *Berdan Ave.*, Wayne, NJ 07470		(+)			65,0	
149	MAGNIFLOC 515C			(+)			50,0	
150	MAGNIFLOC 517C			(+)			40,0	
151	MAGNIFLOC 521C		PAD(1)	(+)			10,0	
152	MAGNIFLOC 570C			(+)			20,0	
153	MAGNIFLOC 571C			(+)			20,0	
154	MAGNIFLOC 572C			(+)			20,0	
155	MAGNIFLOC 573C		PQR(1)	(+) 70%	-5.10^4		20,0	
156	MAGNIFLOC 575C			(+)			20,0	
157	MAGNIFLOC 577C		PQR(1)	(+)	high		20,0	
158	MAGNIFLOC 579C			(+)			20,0	
159	MAGNIFLOC 581C		(1)	(+)	high		20,0	
160	MAGNIFLOC 583C			(+)			50,0	
161	MAGNIFLOC 584C			(+)			100,0	
162	MAGNIFLOC 585C			(+)			50,0	
163	MAGNIFLOC 586C			(+)			100,0	
164	MAGNIFLOC 587C			(+)			50,0	
165	MAGNIFLOC 588C			(+)			100,0	
166	MAGNIFLOC 589C			(+)			70,0	
167	MAGNIFLOC 590C			(+)			100,0	
168	MAGNIFLOC 591C			(+)			50,0	
169	MAGNIFLOC 592C			(+)			25,0	
170	MAGNIFLOC 593C			(+)			80,0	
171	MAGNIFLOC 843A			(-)			1,0	
172	MAGNIFLOC 844A			(-)			1,0	
173	MAGNIFLOC 845A			(-)			1,0	
174	MAGNIFLOC 846A			(-)			1,0	
175	MAGNIFLOC 847A			(-)			1,0	
176	MAGNIFLOC 848A			(-)			1,0	
177	MAGNIFLOC 860A			(-)			1,0	
178	MAGNIFLOC 971N			(0)			1,0	
179	MAGNIFLOC 972N			(0)			1,0	
180	MAGNIFLOC 985N			(0)			1,0	
181	MAGNIFLOC 990N			(0)			1,0	
182	MAGNIFLOC 1848A			(-)			4,0	with activator 478 in ratio 10:1
183	MAGNIFLOC 1849A		(1)	(-) low	high		4,0	
184	MAGNIFLOC 1985N			(0)			4,0	With activator 478 in ratio 10:1
185	MAGNIFLOC 1986N		(1)	(0)	high		4,0	
186	METALENE COAGULANT P6	*Metalene Chem.* Co., Bedford, OH 44014					5,0	
187	MOGUL-CO-940	The Mogel Corp., Chargin Falls, OH 44022					10,0	
188	MOGUL-CO-941						10,0	
189	MOGUL-CO-982						1,5	
190	MOGUL-CO-983						50,0	
191	MOGUL-CO-984						50,0	
192	MOGUL-CO-985						3,5	
193	MOGUL-PC-1901A						1,0	
194	MOGUL-PC-1905A						4,0	
195	MOGUL-PC-1911C						10,0	
196	MOGUL-PC-1913C						40,0	
197	MOGUL-PC-1914C						20,0	
198	MOGUL-PC-1921N						1,0	
199	MOGUL-PC-1943N						1,0	
200	MOGUL-PC-1945C						1,0	
201	MOGUL-PC-1946C						1,0	
202	MOGUL-PC-1950						3,5	
203	MOGUL-6913A						125,0	
204	MOGUL-6921C						40,0	
205	MOGUL-6903C						10,0	
206	MOGUL-7903C						10,0	
207	MOGUL-7913A						125,0	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE AVE. mg/l	MAX. DOSAGE MAX. mg/l	COMMENTS
208	MOGUL-9001A						1,0	
209	MOGUL-9003C						10,0	
210	MOGUL-9013A						125,0	
211	MOGUL-9021C						50,0	
212	MOGUL-9023N						100,0	
213	MOGUL-9025N						1,0	
214	MOGUL-9032C						20,0	
215	MOGUL-9035A						4,0	
216	MOGUL-9036N						4,0	
217	MOGUL-9043N						1,0	
218	MOGUL-9044A						1,0	
219	MOGUL-9045C						1,0	
220	MOGUL-9046C						1,0	
221	*MRL-22*	*Celanese Polymer* Specialities Co.					2,0	
222	Nalcolyte 110A	Nalco Chem. Co., 2901 Butter field Rd., Oakbrook, IL 60521	(s)	(0)	$>10^6$		5,0	
223	Nalcolyte 671			(0)			1,0	
224	Nalcolyte 7870						1,0	
225	Nalcolyte 8100						20,0	
226	Nalcolyte 8101			(+)			10,0	
227	Nalcolyte 8102						50,0	
228	Nalcolyte 8103						10,0	
229	Nalcolyte 8104						10,0	
230	Nalcolyte 8105						20,0	
231	Nalcolyte 8106						30,0	
232	Nalcolyte 8113						10,0	
233	Nalcolyte 8114						10,0	
234	Nalcolyte 8142						5,0	
235	Nalcolyte 8143						10,0	
236	Nalcolyte 8170						1,0	
237	Nalcolyte 8171		(1)	(0)	$>10^6$		1,0	
238	Nalcolyte 8172						1,0	
239	Nalcolyte 8173						1,0	
240	Nalcolyte 8174			(-)	$>3,10^6$		1,0	
241	Nalcolyte 8175						1,0	
242	Nalcolyte 8180						1,0	
243	Nalcolyte 8182						1,0	
244	Nalcolyte 8184						1,0	
245	Nalcolyte 8780						5,0	
246	Nalcolyte 8781						1,0	
247	Nalcolyte 8783						1,0	
248	Nalcolyte 8784						1,0	
249	Nalcolyte 8790						20,0	
250	Nalcolyte 8791						10,0	
251	Nalcolyte 8792						50,0	
252	Nalcolyte 8793						10,0	
253	Nalcolyte 8794						10,0	
254	Nalcolyte 8795						20,0	
255	Nalcolyte 8796						30,0	
256	NALCO 600-SS1						10,1	
257	No 102 Kleer-Floc	Henry W. Fink & Co., 6900 Silverton Ave., Cincinnati, OH 45236					1,0	
258	No 109 Kleer-Floc						1,0	
259	No 116 Kleer-Floc						5,0	
260	No 119 Kleer-Floc						1,0	
261	No 730 Kleer-Floc						1,0	
262	No 735 Kleer-Floc						1,0	
263	O'B FLOC	O'Brien Ind. Inc., 95 Dorsa Ave., Livingston, NJ 07039					10,0	
264	OLIN 4500	Olin Water Services., OLIN Corp., 3155 Fiberglas Rd., Kansas City, KS 66115					1,0	
265	OLIN 4502						1,0	
266	OLIN 4515						1,0	
267	OLIN 4517						1,0	
268	OLIN 5108						20,0	
269	OLIN 5109						10,0	
270	OLIN 5110						5,0	
271	OXFORD-HYDRO-FLOC	Oxford Che. Div., Consolidated Foods Corp., P.O. Box 80202 Atlanta, GA 30341					10,0	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE		COMMENTS
						AVE. mg/l	MAX. mg/l	
272	PEI-600	Dow Chemical USA, Barstow Bld., 2020 Dow Centre Midland, MI 48640	PEI(1)	(+)	$\sim 5.10^4$		5,0	
273	PEI-1090		PEI(1)	(+)			5,0	
274	PERCHEM 550	Pearl River Chem. Co., PO Box 1202 Slidell, LA 70459					50,0	
275	PERCOL LT-20	Allied Colloids, Inc. One Robinson Lane, Ridgewood, NJ 07410	PAC(s)	(0) 0%	$>7.10^6$		1,0	
276	PERCOL LT-22		PAC(s)	(+) 30%	$>7.10^6$		1,0	
277	PERCOL LT-24		PAC(s)	(+) 10%	$>7.10^6$		5,0	
278	PERCOL LT-25		PAC(s)	(-) 30%	$>7.10^6$		5,0	
279	PERCOL LT-26		PAC(s)	(-) 40%	$>7.10^6$		1,0	
280	PERCOL LT-27		PAC				1,0	
281	PERCOL LT-28		PAC				1,0	
282	PERFECTAMYL A5114/2	Frank Herzl Corp., 150 East 58th St., New York, NY 10022	Starch	(0)	$> 10^6$		10,0	
283	POLY-FLOC 4D	Betz Lab. Inc., Somerton Rd., Trevose, PA 19047					25,0	
284	POLY-FLOC 3						30,0	
285	POLYHALL M-295-P.W.	Celanese Polymer Specialities Co., PO Box 99038, Jeffersontown, KY 40299					1,0	
286	POLYMER M-502	Calgon Corp., PO Box 1346 Pittsburgh, PA 15222					5,0	
287	PURIFLOC A-22	Dow Chem. (USA) Barstow Bldg., 2020 Dow Center, Midland MI 48640	PAC				1,0	
288	PURIFLOC A-23 (PWG)		PAC				1,0	
289	PURIFLOC C-31		PEI	(+)	$\sim 3.10^4$		5,0	
290	PURIFLOC N-17		PAC				1,0	
291	PURIFLOC N-20						1,0	
292	SEPARAN AP-30		PAC(s)	(-) 30%	-2.10^6		1,0	
293	SEPARAN AP-273 (Premium)		PAC(s)	(-) 30%	3.10^6		1,0	
294	SEPARAN NP-10 (PWG)		PAC(s)	(-) 5%	$- 10^6$		1,0	
295	SPEEDIFLOC 1	Commercial Chem., 103 Pleasant Ave., Upper Saddle River, NJ 07458					10,0	
296	SPEEDIFLOC 2						5,0	
297	SPLIT	DuBois Chem. Div., WR. Grace & Co., 3630 E. Kemper Rd., Sharonville, OH 45241					19,0	
298	SUPERCOL Guar Gum	General Mills Chem., 4620 W. 77th St., Minneapolis, MN 55435					10,0	
299	TFL 324	Tretolite Div., Petrolite Corp., 369 Marshall Ave., St. Louis, MO 63119					5,0	
300	TOLFLOC 333						7,0	
301	TOLFLOC 334						10,0	
302	TOLFLOC 350						1,0	
303	TOLFLOC 351						1,0	
304	TOLFLOC 355						1,0	
305	TOLFLOC 356						1,0	
306	TOLFLOC 357						1,0	
307	TIDE-TRO	Tidelands Chem., P.O. Box 487 Westlake, LA 70669					7,0	
308	TIDE-TRO B						50,0	
309	TIDE-TRO B-1						5,0	
310	VARCO-FLOC	James Varley and Sons Inc., 1200 Switzer Ave., St. Louis, MO 63147					150,0	
311	WISPROFLOC P	W.A. Scholten's Chemiche, Fabricken B.V., Foxhol, Posthus 1.	Starch				5,0	
312	XD-7817	Dow Chem. USA, Barstow Bldg., 2020 Dow Center, Midland, MI 48640					1,0	
313	XFS-4145L						5,0	
314	XFS-4192 L						5,0	
315	ZETA LYTE (TM) 1C	C-E Minerals, Combustion Eng. Inc., 901 E 8th Ave., King of Prussia PA 19406					5,0	
316	ZETA LYTE (TM) 2C						10,0	
317	ZETA LYTE (TM) 3C						65,0	
318	ZETA LYTE (TM) 4C						10,0	
319	ZETA LYTE (TM) 5C						10,0	

	PRODUCT	MANUFACTURER OR SUPPLIER	TYPE	CHARGE TYPE AND DENSITY	MOL. WT.	MAX. DOSAGE AVE. mg/l	MAX. DOSAGE MAX. mg/l	COMMENTS
320	ZETA LYTE (TM) IA						4,0	
321	ZETA LYTE (TM) ZA						1,0	
322	ZETA FLOC (R) WA						20,0	
323	ZETA FLOC (R) WA (Special)						70,0	
324	ZETA FLOC (R) WA 500						50,0	
325	ZETA FLOC (R) WA 1000						50,0	
326	ZETA FLOC (R) WA 3000						33,3	
327	ZIMMITE ZC-301	Zimmite, Inc., 810 Sharon Drive, Westlake, OH 44145					130,0	
328	ZIMMITE ZT-600						1,0	
329	ZIMMITE ZT-601						1,0	
330	ZIMMITE ZT-603						1,0	
331	ZM-130						80,0	
332	ZM-137						33,0	
333	ZT-616						40,0	
334	ZT-621						80,0	
335	ZT-622						20,0	
336	ZT-623						80,0	
337	ZT-624						20,0	
338	ZT-625						30,0	
339	ZT-626						40,0	
340	ZT-627						80,0	
341	ZT-628						20,0	
342	ZT-637						1,0	
343	ZT-644						1,0	
344	ZT-651						1,0	
345	ZT-657						1,0	
346	ZT-661						1,0	
347	ZT-669						4,0	
348	ZT-680						10,0	
349	ZT-684						20,0	
350	ZT-686						20,0	
351	ZUCLAR 110 PW	Fabcon Int., 1275 Columbus Ave., San Francisco, CA 94133					0,5	

A.3 READY REFERENCE GUIDE TO COAGULATION AND FLOCCULATION APPLICATIONS

The following table presents summarized information on the application of metal coagulants alone; with flocculant aids or with polyelectrolytes as primary coagulants principally in the area of water and wastewater treatment. The information has been selectively gleaned from the literature to provide a reasonably wide range of applications.

It is realised that such listed information cannot substitute for an extensive testing program to assess the most practicable and economical conditions for coagulation and flocculation applied to a particular water. However, for a given application, which may superficially at least fall into one of the listed water types and constituents, a variety of possible treatment alternatives will be obtained. Obviously, since each water type from which the data was obtained cannot be fully characterised in such a table, the information gleaned cannot be used as design criteria or to predict a treatment system for a particular water.

The objective of the listed information is to provide a first stage indication of some likely treatment alternatives for a particular application which, it is hoped, may prove useful as a first step in planning an experimental and/or feasibility program. The alternatives listed do not preclude other treatment solutions.

The existence or absence of a particular entry in the Table depends on available information from either the references cited or by manufacturers/suppliers of chemicals. In cases where there is a possibility of the reader entering certain information at a later stage (principally those entries describing polyelectrolyte characteristics) the relevant entries have been left blank for this purpose.

For the entries related to polyelectrolyte molecular weights, where information from the manufacturer is not available, in some cases an indication is provided such that low, high, very high and ultra high usually refer to molecular weights in the ranges 0 to 10^6; 10^6 to 3.10^6; 3.10^6 to 8.10^6 and 8.10^6 to 15.10^6 respectively. In the case of metal coagulants, an entry in the molecular weight column indicates the product formula; For example, an entry for aluminium sulphate (alum) of ~630 indicates that the chemical $Al_2(SO_4)_3.16H_2O$ was used (or, in some cases, assumed).

With the entries for mixing conditions, where two figures appear this signifies rapid mix and slow mix values; For example, a rapid mix period of 2 minutes followed by a slow (flocculation) period of 30 minutes is entered thus: 2/30. This also applies to G value entries.

Abbreviations used in the Table are as follows:

% ABS = percentage absorbance value
APHA = American Public Health Association Methodology
Cat. = cationic
FTU = turbidity units standardized against formazin suspensions ("Hach" methodology)
JTU = Jackson turbidity units
OD = optical density measurements
PAC = polyacrylamide or acrylamide/acrylate based polyelectrolyte
PAM = polyamine
PDADMAC = polydiallyldimethylammonium chloride
PEI = polyethylenimine
pfu/ml = plaque forming units per ml sample
Pt-Co = colour value standardized against platinum-cobalt standard solutions
TOC = total organic carbon
TSS = total suspended solids
TU = unspecified turbidity units
U/S = unspecified
UV Spec = spectrophotometer absorbance values in the ultraviolet range

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE $mg\ l^{-1}$	ELEC. MOBILITY µ/s/v/cm	STREAM. CURRENT µA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM. %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN		INITIAL	FINAL			INITIAL	FINAL		
1	Turbidity	—	(Synthetic) Kaolin suspension	Alum	—	~600	5	0,45	7,7	—	—	—	—	−1,2	—	—	U/S	2/30	—	—	mg/l	65,8	U/S	90	—	—	—	Settled jar test	5
2	Turbidity	—	(Synthetic) Kaolin suspension	Alum.	—	~600	5	0,45	7,7	Act. Silica	—	—	1,0	−1,4	—	—	U/S	2	—	2/30	mg/l	65,8	U/S	92	—	—	—	Settled jar test	5
3	Turbidity	—	(Synthetic) Kaolin suspension	Alum.	—	~600	50	4,5	7,5	—	—	—	—	—	—	—	1000/20	0,25/30	—	—	FTU	40	1,6	—	—	—	—	Settled Batch ("Jar") Test	13
4	Turbidity	—	(Synthetic) Kaolin suspension	Ferric Sulphate	—	~525	5	1,07	7,0	—	—	—	—	−1,5	—	—	U/S	2/28	—	—	mg/l JTU	74,0 294,0	U/S	— 97	—	—	—	Settled jar test	8
5	Turbidity	—	(Synthetic) Kaolin suspension	NaCl	—	—	5.10^{-3} M		4	—	—	—	—	ζ = ~ −10 mV	—	—	U/S	U/S	—	—	JTU	20	6,5	—	—	—	—	Sand filtration	31
6	Turbidity	—	(Synthetic) Kaolin suspension	NaCl/ $CaCl_2$	—	—	5.10^{-3} M 5.10^{-4} M		4	—	—	—	—	ζ = ~ −10 mV	—	—	U/S	U/S	—	—	JTU	20	3,5	—	—	—	—	Sand filtration	31
7	Turbidity	—	(Synthetic) Kaolin suspension	NaCl/ $MgCl_2$	—	—	5.10^{-3} M 5.10^{-4} M		4	—	—	—	—	ζ = ~ −10 mV	—	—	U/S	U/S	—	—	JTU	20	4,5	—	—	—	—	Sand filtration	31
8	Turbidity	Colour	(Synthetic) Bentonite suspension	Ferric Sulphate	—	~525	12	2,6	U/S	—	—	—	—	—	−11,0	—	U/S	U/S	—	—	JTU	5	1	—	Pt - Co	20	5	Settled jar test	47
9	Turbidity	Colour	(Synthetic) Bentonite suspension	Ferric Sulphate	—	~525	23	4,9	U/S	—	—	—	—	—	−5,0	—	U/S	U/S	—	—	JTU	15	1	—	Pt - Co	15	5	Settled jar test	47
10	Turbidity	—	(Synthetic) Bentonite suspension	Alum.	—	~600	45	4,0	7,0	—	—	—	—	—	—	—	U/S	U/S	—	—	JTU	200	20	—	—	—	—	Settled jar test	4
11	Turbidity	—	(Synthetic) Kaolin suspension	Calcium Chloride	—	—	250	—	7	Anionic PAC	4%	$\sim 5.10^{6}$	0,24	−0,4	—	—	U/S	5	U/S	20/20	mg/l JTU	33,4 37	U/S 5	—	—	—	—	Settled jar test	9
12	Turbidity	—	(Synthetic) Kaolin suspension	Calcium Chloride	—	—	250	—	7	Anionic PAC	30%	$\sim 5.10^{6}$	0,012	−0,6	—	—	U/S	5	U/S	20/20	mg/l JTU	33,3 34	U/S 5	—	—	—	—	Settled jar test	9
13	Turbidity	—	(Synthetic) Kaolin suspension	Cat. PDADMA	—	$\sim 5\ 10^{4}$	0,03 to 0,145	—	—	—	—	—	—	0 to −0,7	—	—	U/S	20/20	—	—	mg/l JTU	15-73 20-110	U/S 12-2	—	—	—	—	Settled jar test	9
14	Turbidity	—	Kaolin + Bentonite (conc. ratio 1:2)	Alum.	—	~600	20	1,8	U/S	—	—	—	—	—	—	—	U/S	05/5	—	—	mg/l JTU	6 —	U/S 0,2	—	—	—	—	Sand filtration	44

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT	DOSAGE $mg\ l^{-1}$	ELEC. MOBILITY μ/s/v/cm	STREAM. CURRENT μA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM. %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
15	Turbidity	—	Kaolin + Bentonite (conc. ratio 1:2)	Cat. PDADMAC (Catfloc)			1,0	—	—	—	—	—	—	—	—	—	U/S	0,5/5	—	—	mg/l JTU	6 —	U/S 0,2	—	—	—	—	Dual Media Direct filt.	44
16	Turbidity	—	Kaolin + Bentonite (conc. ratio 1:2)	Cat. PDADMAC (Catfloc T)			3,0	—	—	—	—	—	—	ζ=+7,4 mV	—	—	90	9,2	—	—	mg/l FTU	60 32	U/S ~0,06	—	—	—	—	Dual Media Direct filt.	43
17	Turbidity	—	Montmorillonite suspension	Alum.	—	~600	15	1,4	7,8	—	—	—	—	-1,7	—	—	U/S	2/30	—	—	mg/l	65,6	U/S	95	—	—	—	Settled jar test	5
18	Turbidity	—	Montmorillonite suspension	Ferric Sulphate	—	~525	5	1,07	6,5	—	—	—	—	-1,8	—	—	U/S	2/28	—	—	mg/l JTU	62,0 58,0	U/S	— 95	—	—	—	Settled jar test	8
19	Turbidity	—	Montmorillonite suspension	Cat. Poly-4 vinyl-N-Methyl-pyridonium iodide		$3,3.10^{5}$	0,5	—	8,0 (not opt)	—	—	—	—	- ,3	—	—	U/S	5/25	—	—	mg/l OD	150 0,7	— 0,01	—	—	—	—	Settled jar test	36
20	Turbidity	—	Fullers Earth suspension	Alum.	—	~600	5	0,45	7,7	—	—	—	—	-0,5	—	—	U/S	2/30	—	—	mg/l	72,2	U/S	90	—	—	—	Settled jar test	5
21	Turbidity	—	Fullers Earth suspension	Alum.	—	~600	50	4,5	7,0	—	—	—	—	—	—	—	U/S	U/S	—	—	JTU	200	20	—	—	—	—	Settled jar test	4
22	Turbidity	—	Fullers Earth suspension	Ferric Sulphate	—	~525	5	1,07	6,7	—	—	—	—	-1,3	—	—	U/S	2/28	—	—	mg/l JTU	64,8 79,0	U/S	97	—	—	—	Settled jar test	8
23	Turbidity	—	(Synthetic) SiO_2 Silica suspension	Alum	—	~600	10	0,9	7,0	—	—	—	—	—	—	0	U/S	U/S	—	—	mg/l	100	~2,0	—	—	—	—	Settled jar test	48
24	Turbidity	—	(Synthetic) SiO_2 Silica suspension	Alum	—	~600	2,5	0,23	7,2	—	—	—	—	—	—	-5.10^{-4}	U/S	U/S	—	—	mg/l	100	~1,0	—	—	—	—	Sand Filtration	48
25	Turbidity	—	Synthetic Silica susp.	$Fe(ClO_4)_3$ $6H_2O$	—	~460	$1,6.10^{-5}$ M Fe III		2,5 to 7,5	—	—	—	—	—	—	—	U/S	15	—	—	g/l	20	U/S	—	—	—	—	Settled jar test	40
26	Turbidity	U/S	River / lake water	Alum.	—	~600	5	0,45	U/S	—	—	—	—	—	—	—	1000/18	U/S/30	—	—	TU	1 to 3	~0,2	93,6	—	—	—	Sedimentation/Filtration	2
27	Turbidity	U/S	River Water	Alum.	—	~630	205	17,6	6,2	—	—	—	—	ζ=-3,5 mV	—	-2.10^{-3}	U/S	1/20	—	—	FTU	42	0,1	—	—	—	—	Settled jar test	54
28	Turbidity	U/S	River Water	Alum.	—	~630	240	20,6	5,8	—	—	—	—	ζ=+8,5 mV	—	$+8,5.10^{-3}$	U/S	1/20	—	—	FTU	380	5	—	—	—	—	Settled jar test	54

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
							DOSAGE										PRIMARY COAGULANT		FLOCCULANT AID			CONCENTRATION				CONCENTRATION			
				TYPE	CHARGE DENSITY	MOL WT.	mg/l	as Me ion	OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l⁻¹	ELEC MOBILITY µ/s/v/cm	STREAM CURRENT µA	COLLOID CHGE. meq/l	G s⁻¹	TIME MIN.	G s⁻¹	TIME MIN.	UNITS	INITIAL	FINAL	REM %	UNITS	INITIAL	FINAL		
29	*Turbidity*	—	*River Water (Pred. mont. clay)*	*Alum.*	—	~694	20	1,6	~7	—	—	—	—	−0,5 to −1,5	—	—	U/S	U/S	—	—	JTU	~100	U/S	~94	—	—	—	Settled jar test	10
30	Turbidity	—	River Water	Alum.	—	~694	40	3,1	U/S	—	—	—	—	—	—	—	U/S	−/30	—	—	JTU	1000	U/S	99,38	—	—	—	Settled jar test	20
31	Turbidity	—	River Water	Alum.	—	~694	20	1,6	U/S	—	—	—	—	—	—	—	U/S	−/30	—	—	JTU	98	U/S	96,2	—	—	—	Settled jar test	20
32	Turbidity	—	River Water	Alum.	—	~694	20	1,6	U/S	U/S Cationic	—	—	6	—	—	—	U/S	1	U/S	−/30	JTU	98	U/S	97,3	—	—	—	Settled jar test	20
33	Turbidity	—	River Water	Alum.	—	~694	40	3,1	U/S	U/S Cationic	—	—	6	—	—	—	U/S	1	U/S	−/30	JTU	1000	U/S	99,53	—	—	—	Settled jar test	20
34	Turbidity	—	Pond Water	Alum.	—	~694	30	2,3	U/S	U/S Cationic	—	—	2	—	—	—	U/S	1	U/S	−/30	JTU	300	U/S	99,53	—	—	—	Settled jar test	20
35	Turbidity	U/S	River/Lake Water	Alum.	—	~600	4,0	0,4	U/S	Cat. QAC (Catfloc T)			0,2	—	—	—	1000	U/S	1000/18	U/S/30	TU	1 to 3	~0,2	93	—	—	—	Sedimentation/ Filtration	2
36	Turbidity	U/S	River/Lake Water	Cat PDADMAC (Catfloc T)			0,4	—	—	—	—	—	—	—	—	—	1000/18	U/S/30	—	—	TU	1 to 3	~0,2	93,5	—	—	—	Sedimentation/ Filtration	2
37	Turbidity	Low Colour	River Water	Cat PDADMAC (Catfloc B)		$<10^6$	1,0	—	—	—	—	—	—	—	—	—	~700/45	U/S/30	—	—	JTU	5	1,25	—	Colour Removal poor			Sedimentation	35
38	Turbidity	Low Colour	River Water	Cat PDADMAC (Catfloc B)		$<10^6$	1,0	—	—	—	—	—	—	—	—	—	450/45	U/S/30	—	—	JTU	135 to 270	0,43	—	Colour Removal poor			Sedimentation	35
39	Turbidity	U/S	Lake Water	Cat. PDADMAC (Catfloc T)			5,0	—	—	—	—	—	—	ζ=+7,5 mV	—	—	U/S	15	—	—	FTU	1,9 to 3,6	0,05	—	—	—	—	Direct Filtration	30
40	Turbidity	U/S	Lake Water	Cat. (Nalcolyte 607)			12,5	—	—	—	—	—	—	ζ=+12,5 mV	—	—	U/S	15	—	—	FTU	~2,0	0,05	—	—	—	—	Direct Filtration	30
41	Turbidity	U/S	Lake Water	Cat. (Nalcolyte 8101)			10,0	—	—	—	—	—	—	ζ=+15 mV	—	—	U/S	15	—	—	FTU	~2,0	0,05	—	—	—	—	Direct Filtration	30
42	Turbidity	U/S	Lake Water	Cat. Magnifloc 570-C)			6,0	—	—	—	—	—	—	ζ=+12,5 mV	—	—	U/S	15	—	—	FTU	2,0 to 2,3	0,05	—	—	—	—	Direct Filtration	30

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l^{-1}	ELEC. MOBILITY μ/s/v/cm	STREAM CURRENT μA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM. %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
43	Organic Colour	—	(Synthetic) Humic Acid Solution	Alum. Chloride	—	—	4,5 . 10^{-4}M		5,3	—	—	—	—	ζ=+27mV	—	—	U/S	1/15	—	—	mg/l	25	4,3	—	—	—	—	Filtered jar test	23
44	Organic Colour	—	(Synthetic) Humic Acid Solution	Alum. Nitrate	—	reagent grade	2,5 . 10^{-3}M		9,5	—	—	—	—	—	—	—	U/S	-/10	—	—	mg/l	50	—	99	—	—	—	Settled jar test	33
45	Organic Colour	—	(Synthetic) Humic Acid Solution	Alum.	—	~695	97,7 μe/l		6,0	—	—	—	—	—	—	—	U/S	U/S	—	—	mg/l	50	—	—	—	—	—	Settled jar test	37
46	Organic Colour	—	(Synthetic) Fulvic Acid Solution	Alum.	—	~695	90 μe/l		5,8	—	—	—	—	—	—	—	U/S	U/S	—	—	mg/l	50	—	—	—	—	—	Settled jar test	37
47	Organic Colour	—	(Synthetic) Humic Acid	Alum.	—	~695	250	19	6,0 (not opt)	—	—	—	—	—	—	—	U/S	2/20	—	—	mg/l	50	—	70	—	—	—	Settled jar test	22
48	Organic Colour	—	(Synthetic) Humic Acid	Alum.	—	~695	10	0,7	6,0 (not opt)	Nonionic Nalcolyte (8171)		>10^{6}	1,0	—	—	—	U/S	2	U/S	0,5/20	mg/l	5	—	97	—	—	—	Settled jar test	22
49	Organic Colour	—	(Synthetic) Fulvic Acid	Ferric chloride	—	~270	55	11	7,2	—	—	—	—	—	—	—	U/S	1/15	—	—	mg/l	10	2,5	—	—	—	—	Filtered jar test	23
50	Organic Colour	—	(Synthetic) Humic Acid Solution	Cat. PEI (Purifloc C - 31)		3.10^{4}	2,2	—	4,0	—	—	—	—	—	—	—	U/S	U/S	—	—	mg/l	10	0,2	—	—	—	—	Settled jar test	37
51	Organic Colour	—	(Synthetic) Humic Acid Solution	Cat. Poly-4-Vinyl-N-Methylpyridonium iodide		3,3.10^{5}	13	—	8,0 (Not opt.)	—	—	—	—	0	—	—	U/S	5/25	—	—	mg/l	10	0,1	—	—	—	—	Settled jar test	36
52	Organic Colour	—	(Synthetic) Fulvic Acid Solution	Cat. Poly-4-Vinyl-N-Methylpyridonium iodide		3,3.10^{5}	27	—	8,0 (Not opt)	—	—	—	—	+ 0,4	—	—	U/S	5/25	—	—	mg/l	50	0,1	—	—	—	—	Settled jar test	36
53	Organic Colour	Montmorillonite Clay	Fulvic Acid Turbid Water	Cat. Poly-4-Vinyl-N-Methylpyridonium iodide		3,3.10^{5}	30	—	8,0 (Not opt.)	—	—	—	—	+ 0,3	—	—	U/S	5/25	—	—	mg/l	50	1,0	—	mg/l OD	150 0,65	— 0,1	Settled jar test	36
54	Organic Colour	—	(Synthetic) Humic Acid	Cat. PDADMAC (Catfloc B)		<10^{6}	40	—	6,0	—	—	—	—	+ 1,0	—	—	U/S	2/20	—	—	mg/l	10	—	96	—	—	—	Settled jar test	22
55	Organic Colour	—	(Synthetic) Fulvic Acid	Cat. (Primafloc C 7)			10	—	6,0	—	—	—	—	—	—	—	U/S	1/15	—	—	mg/l	10	—	87	—	—	—	Settled jar test	41
56	Organic Colour	Turbidity	River Water	Alum.	—	~600	200	18	5,0	—	—	—	—	—	—	—	U/S	2/20	—	—	U/S units	446	15	—	mg/l	19	U/S	Settled jar test	7

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l⁻¹	ELEC. MOBILITY μ/s/V/cm	STREAM. CURRENT μA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s⁻¹	TIME MIN.	G s⁻¹	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
57	Organic Colour	—	River Water	Alum.	—	~695	55	4,3	5,2	—	—	—	—	+0,05	—	—	U/S	2/20	—	—	mg/l Pt-Co	225	10	—	—	—	—	Settled jar test	6
58	Organic Colour	Turbidity	River Water	Alum.	—	~600	20	1,6	U/S	—	—	—	—	—	−3,0	—	U/S	U/S	—	—	U/S units	25	5	—	JTU	2	0,1	Settled jar test	47
59	Organic Colour	Turbidity	River Water	Alum.	—	~600	35	3,2	U/S	—	—	—	—	—	+0,5	—	U/S	U/S	—	—	U/S units	35	5	—	JTU	1	0,1	Settled jar test	47
60	Organic Colour	—	Lake Water	Alum.	—	~570	90	9	5,6	—	—	—	—	—	—	—	U/S	0,5/15	—	—	UV Spec	0,65	0,04	—	—	—	—	Settled jar test	14
61	Organic Colour	—	Lake Water	Alum.	—	~600	50	4,5	5,5	Sodium Aluminate	—	—	10	—	—	—	U/S	U/S	U/S	U/S	UV Spec	~0,60	~0,1	—	—	—	—	Sedimentation + Filtration	12
62	Organic Colour	—	Lake Water	Alum.	—	~570	90	9	5,6	Cat PAC (Magnafloc LT-24)	10%	>7.10⁶	0,7	—	—	—	U/S	0,5/15	—	—	UV Spec	0,65	0,03	—	—	—	—	Settled jar test	14
63	Organic Colour	Turbidity	River Water	Ferric Sulphate	—	~725	103	16	3,5	—	—	—	—	0	—	—	U/S	2/20	—	—	U/S units	446	9	—	mg/l	19	U/S	Settled jar test	7
64	Organic Colour	—	Lake Water	Ferric Sulphate	—	~725	65	10	4,0	—	—	—	—	—	—	—	U/S	0,5/15	—	—	UV Spec	0,65	0,18	—	—	—	—	Settled jar test	14
65	Organic Colour	—	Lake Water	Ferric Sulphate	—	~725	65	10	4,0	Cat PAC (Magnafloc LT-24)	10%	>7.10⁶	0,6	—	—	—	U/S	0,5/15	—	—	UV Spec	0,65	0,15	—	—	—	—	Settled jar test	14
66	Organic Colour	—	Lake Water	Ferric Chloride	—	~163	23	8	4,0	—	—	—	—	—	—	—	U/S	0,5/15	—	—	UV Spec	0,65	0,15	—	—	—	—	Settled jar test	14
67	Organic Colour	—	Lake Water	Ferric Chloride	—	~163	23	8	4,0	Cat PAC (Magnafloc LT 24)	10%	>7.10⁶	0,6	—	—	—	U/S	0,5/15	—	—	UV Spec	0,65	0,13	—	—	—	—	Settled jar test	14
68	Organic Colour	—	River Water	Ferric Sulphate	—	~555	60	12	4,1	—	—	—	—	−0,3	—	—	U/S	2/20	—	—	mg/l Pt-Co	225	5	—	—	—	—	Settled jar test	6
69	Bacteria (E. Coli)	—	Pure Culture 2,5.10⁷ cells/ml	Cat PEI Borden		3.5.10⁴	0,7	—	7,0	—	—	—	—	$\zeta = -14{,}25$ mV	—	—	U/S	2/60	—	—	Refiltration rate 1,0 cm³/s			—	—	—	—	Refiltration jar test	53
70	Bacteria (E. Coli)	—	Pure Culture 2,5.10⁷ cells/ml	Cat PEI DOW		~6.10⁴	0,5	—	7,0	—	—	—	—	$\zeta = -14{,}25$ mV	—	—	U/S	2/60	—	—	Refiltration rate 1,4 cm³/s			—	—	—	—	Refiltration jar test	53

	PRINCIPAL CONSTITUENT REQUIRING REMOVAL	OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID (S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
				TYPE	CHARGE DENSITY	MOL WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l^{-1}	ELEC. MOBILITY μ/s/v/cm	STREAM CURRENT μA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
71	Algae (Chlorella vulgaris)	—	Stabilization pond effluent	Alum.	—	~630	290	25	5,5	—	—	—	—	—	—	—	U/S	0,25	—	—	Nephelometer units	~100	18,5	—	—	—	—	Dissolved air flotation	11
72	Algae (Chlorella vulgaris)	—	Stabilization pond effluent	Ferric Sulphate	—	~506	227	50	5,8	—	—	—	—	—	—	—	U/S	0,25	—	—	Nephelometer units	~100	10	—	—	—	—	Dissolved air Flotation	11
73	Algae (Chlorella vulgaris)	—	Stabilization pond effluent	Ferric Chloride	—	~162	145	50	5,7	—	—	—	—	—	—	—	U/S	0,25	—	—	Nephelometer units	~100	5	—	—	—	—	Dissolved air Flotation	11
74	Algae (Chlorella ellipsoidea)	—	Pure Culture	Cat. PEI (DOW)		$2,1.10^4$	60	—	6,2	—	—	—	—	+ 0,6	—	—	U/S	U/S	—	—	mg/l % trans	220 33	— 86	—	—	—	—	Settled jar test.	52
75	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Alum	—	~630	25	2,14	U/S	—	—	—	—	—	—	$+0,8.10^{-3}$	U/S	U/S	U/S	U/S	pfu/ml	7.10^5	10^3	99,9	JTU	3,5	0,15	Settled jar test.	56
76	Viruses (bacteriophage f2)	Turbidity/ COD	Biological filter effluent	Alum.	—	~630	76	6,5	7,1	—	—	—	—	~0	—	~0	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,8	JTU mg/l COD	3,9 61	93,6% 96,7%	Settled jar test.	45
77	Viruses (bacteriophage f2)	Turbidity/ COD	River Water	Alum.	—	~630	15	1,3	6,8	—	—	—	—	-Ve	—	-Ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,45	JTU mg/l COD	1,2 5,3	96,5% 43,0%	Settled jar test	45
78	Viruses (bacteriophage T4 MS2)	Turbidity	Lab. Culture	* Alum.	—	~694	40	3,1	5,24	—	—	—	—	—	—	—	U/S	1/30	—	—	pfu/ml	$4,5.10^5$	U/S	96	JTU	12,5	—	Settled jar test	19
79	Viruses (Polio virus)	Turbidity (Montmorillonite)	Lab. Culture	Alum.	—	~630	10	0,86	6,8	—	—	—	—	—	—	—	U/S	1/29	—	—	pfu/ml	3 to 7. 10^4	U/S	90	mg/l	50	97%	Settled jar test	51
80	Viruses (bacteriophage f2)	Turbidity	Lab Culture	Alum.	—	~630	30	2,6	U/S	Sod. Aluminat. $Na_2O.Al_2O_3$	—	—	23	—	—	+ve	U/S	U/S	U/S	U/S	pfu/ml	$\sim7.10^5$	U/S	98,6	JTU	3,5	96,5%	Settled jar test	56
81	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Alum.	—	~630	18	1,54	U/S	Anionic (Coag Aid 253 Calgon)	med	high	0,1	—	—	~0 (+ve)	U/S	U/S	U/S	U/S	pfu/ml	$\sim7.10^5$	U/S	99,3	JTU	3,5	98%	Settled jar test	56
82	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Alum.	—	~630	16	1,54	U/S	Anionic (Magnifloc 860)			0,1	—	—	~0 (+ve)	U/S	U/S	U/S	U/S	pfu/ml	$\sim7.10^5$	U/S	99,6	JTU	3,5	98,5%	Settled jar test	56
83	Viruses (bacteriophage f2)	Turbidity/ COD	Biological filter effluent	Alum.	—	~630	80	6,86	7,2	Anionic (Coag Aid 253 Calgon)	med	high	0,6	~0 (-ve)	—	~0 (-ve)	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,7	JTU mg/l COD	3,9 61	94% 71%	Settled jar test	45
84	Viruses (bacteriophage f2)	Turbidity/ COD	Biological filter effluent	Alum.	—	~630	75	6,43	7,2	Anionic (Magnifloc 860)			0,4	0	—	—	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,55	JTU mg/l COD	3,9 61	94,8% 50%	Settled jar test	45

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l^{-1}	ELEC. MOBILITY µA/v/cm	STREAM CURRENT µA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM. %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
85	Viruses (bacteriophage f2)	Turbidity / COD	River Water	Alum.	—	~630	10	0,86	6,7	Anionic (Coag. Aid 253 Calgon)	med	high	0,4	+ ve	—	—	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,5	JTU mg/l COD	1,2 5,3	99,65% 97,5%	Settled jar test	45
86	Viruses (bacteriophage f2)	Turbidity/ COD	River Water	Alum.	—	~630	9	0,77	6,8	Anionic (Magnifloc 860)			0,2	+ ve	—	—	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,93	JTU mg/l COD	1,2 5,3	98,7% 79,5%	Settled jar test	45
87	Viruses (bacteriophage T2)	Turbidity	Lab. Culture	Alum.	—	~630	40	3,43	7,0	Anionic (Hercules CMC)			0,5	—	—	—	U/S	1	U/S	1/29	pfu/ml	3 to 7 10^4	U/S	97	mg/l	10	U/S	Settled jar test	51
88	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Alum.	—	~630	18	1,54	U/S	Nonionic Aid 233 (Calgon)			0,4	—	—	0	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	99,3	JTU	3,5	96,7%	Settled jar test	56
89	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Alum.	—	~630	18	1,54	U/S	Nonionic (Magnifloc 971)			1,0	—	—	0	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	99,4	JTU	3,5	98,8%	Settled jar test	56
90	Viruses (bacteriophage f2)	Turbidity / COD	Biological filter effluent	Alum.	—	~630	80	6,86	7,1	Nonionic (Coag. Aid 233 Calgon)			1,0	0	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,9	JTU mg/l COD	3,9 81	97,7% 91%	Settled jar test	45
91	Viruses (bacteriophage f2)	Turbidity/ COD	Biological filter effluent	Alum.	—	~630	80	6,86	6,7	Nonionic (Magnifloc 971)			0,4	0	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,65	JTU mg/l COD	3,9 81	94,7% 61%	Settled jar test	45
92	Viruses (bacteriophage f2)	Turbidity/ COD	River Water	Alum.	—	~630	10	0,86	6,8	Nonionic (Coag Aid 233 Calgon)			0,25	+ ve	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,5	JTU mg/l COD	1,2 5,3	97,4% 59,3%	Settled jar test	45
93	Viruses (bacteriophage f2)	Turbidity/ COD	River Water	Alum.	—	~630	10	0,86	6,8	Nonionic (Magnifloc 971)			0,4	+ ve	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	98,6	JTU mg/l COD	1,2 5,3	97,2% 85 %	Settled jar test	45
94	Viruses (bacteriophage T2)	Turbidity	Lab. Culture	Alum.	—	~630	40	3,43	7,0	Nonionic (Nalcolyte 110)		>10^6	0,5	—	—	—	U/S	1	U/S	1/29	pfu/ml	3 to 7.10^4	U/S	97	mg/l	10	U/S	Settled jar test	51
95	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Alum.	—	~630	18	1,54	U/S	Cat. PDADMAC (Catfloc)			1,0	—	—	~0 (+ve)	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	99,8	JTU	3,5	98,2%	Settled jar test	56
96	Viruses (bacteriophage f2)	Turbidity/ COD	Biological filter effluent	Alum.	—	~630	65	5,6	7,3	Cat. PDADMAC (Catfloc)			1,5	+ ve	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,96	JTU mg/l COD	3,9 81	94,9% 95,5%	Settled jar test	45
97	Viruses (bacteriophage f2)	Turbidity / COD	River Water	Alum.	—	~630	8	0,7	6,8	Cat. PDADMAC (Catfloc)			0,25	~0 (−ve)	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,75	JTU mg/l COD	1,2 5,3	97,4% 49,5%	Settled jar test	45
98	Viruses (bacteriophage T4)	Turbidity	Lab. Culture	Alum.	—	~694	50	3,89	5,3	Cat. PDADMAC (Catfloc)			1,0	—	—	—	U/S	1	U/S	1/29	pfu/ml	4,49. 10^5	U/S	99,9	JTU	12,5	98,9%	Settled jar test	19

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE $mg\ l^{-1}$	ELEC MOBILITY μ/s/v/cm	STREAM CURRENT μA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM. %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN	G s^{-1}	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
99	Viruses (Poliovirus type I)	Turbidity	Lab Culture	Alum.	—	~630	10	0,86	6,8	Cat (Purifloc C 32)			1,0	—	—	—	U/S	1	U/S	1/29	pfu/ml	3 to 7.10^4	U/S	81	mg/l	50	95%	Settled jar test	51
100	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Ferric Sulphate	—	~724	50	7,73	U/S	—	—	—	—	—	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	92	JTU	3,5	89%	Settled jar test	56
101	Viruses (bacteriophage f2)	Turbidity/COD	Biological Filter Effluent	Ferric Sulphate	—	~724	176	27,2	6,5	—	—	—	—	~0 (− ve)	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	98,9	JTU mg/l COD	3,9 81	93% 96,5%	Settled jar test	45
102	Viruses (bacteriophage f2)	Turbidity/COD	River Water	Ferric Sulphate	—	~724	62	9,59	7,2	—	—	—	—	~0 (− ve)	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,91	JTU mg/l COD	1,2 5,3	91% 89%	Settled jar test	45
103	Viruses (Poliovirus type I)	Turbidity	Lab. Culture	Ferric Sulphate	—	~724	11,6	1,79	6,8	—	—	—	—	—	—	—	U/S	1/29	—	—	pfu/ml	3 to 7.10^4	U/S	85	mg/l	50	93%	Settled jar test	51
104	Viruses (Poliovirus type I)	Turbidity	Lab. Culture	Ferric Sulphate	—	~724	11,6	1,79	6,8	Cat (Purifloc C 32)			1,0	—	—	—	U/S	1	U/S	1/29	pfu/ml	3 to 7.10^4	U/S	76	mg/l	50	95%	Settled jar test	51
105	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Ferric Chloride	—	~162	50	17,3	U/S	—	—	—	—	—	—	+ ve	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	99,4	JTU	3,5	92,5%	Settled jar test	56
106	Viruses (bacteriophage f2)	Turbidity/COD	Biological Filter Effluent	Ferric Chloride	—	~162	109	37,7	6,8	—	—	—	—	~0 (+ ve)	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	94,6	JTU mg/l COD	3,9 81	90% 92%	Settled jar test	45
107	Viruses (bacteriophage f2)	Turbidity/COD	River Water	Ferric Chloride	—	~162	40	13,8	6,8	—	—	—	—	~0 (+ ve)	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	99,1	JTU mg/l COD	1,2 5,3	95% 73%	Settled jar test	45
108	Viruses (bacteriophage MS2)	Turbidity	Lab Culture	Ferric Chloride	—	~162	50	17,3	5,0	—	—	—	—	—	—	—	U/S	U/S	U/S	U/S	pfu/ml	3,9. 10^5	U/S	99	JTU	~15	~97%	Settled jar test	34
109	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Cat (Drewfloc 21)			2,0	—	—	—	—	—	—	—	—	~0 (− ve)	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	76	JTU	3,5	40%	Settled jar test	56
110	Viruses (bacteriophage f2)	Turbidity	Lab. Culture	Cat. PDADMAC (Catfloc)			2,0	—	—	—	—	—	—	—	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	~7.10^5	U/S	99,6	JTU	3,5	72%	Settled jar test	56
111	Viruses (bacteriophage f2)	Turbidity/COD	Biological Filter Effluent	Cat. PDADMAC (Catfloc)			5,4	—	7,3	—	—	—	—	U/S	—	U/S	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	70	JTU mg/l COD	3,9 81	~0% 17%	Settled jar test	45
112	Viruses (bacteriophage f2)	Turbidity/COD	River Water	Cat. PDADMAC (Catfloc)			2,2	—	7,5	—	—	—	—	U/S	—	~0 (+ ve)	U/S	U/S	U/S	U/S	pfu/ml	U/S	U/S	92,1	JTU mg/l COD	1,2 5,3	46% 26%	Settled jar test	45

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
																	PRIMARY COAGULANT		FLOCCULANT AID										
				TYPE	CHARGE DENSITY	MOL WT.	DOSAGE mg/l	DOSAGE as Me ion	OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l⁻¹	ELEC. MOBILITY μ/s/v/cm	STREAM CURRENT μA	COLLOID CHGE. meq/l	G s⁻¹	TIME MIN.	G s⁻¹	TIME MIN	UNITS	CONCENTRATION INITIAL	CONCENTRATION FINAL	REM %	UNITS	CONCENTRATION INITIAL	CONCENTRATION FINAL		
113	Viruses (bacteriophage MS2)	Turbidity/COD etc	Activated sludge plant effluent	Cat. PAM (DOW) (Purifloc C-31)		6.10^4	0,4 mg/g D. E.		8,0	—	—	—	—	—	—	—	U/S	U/S	U/S	U/S	pfu/ml	$6,6.10^4$	U/S	97	U/S	U/S	U/S	Diat. Earth. Filter	1
114	Micro-organisms	—	Activated sludge	Alum.	—	~695	200	15,6	5,4	—	—	—	—	—	—	—	U/S	U/S/15	—	—	mg/l COD Cells/ml	~600 $2,7.10^8$	120 $0,1.10^8$	—	—	—	—	Settled jar test	49
115	Micro-organisms	—	Activated sludge	Ferric Sulphate	—	~507	150	33	5,0	—	—	—	—	—	—	—	U/S	U/S/15	—	—	mg/l COD Cells/ml	~600 $2,7.10^8$	80 $0,02.10^8$	—	—	—	—	Settled jar test	49
116	Micro-organisms	—	Activated sludge	Cat. (Purifloc 602)			50	—	5,0	—	—	—	—	—	—	—	U/S	U/S/15	—	—	mg/l COD	~1000	250	—	—	—	—	Settled jar test	49
117	Micro-organisms	—	Activated sludge	Cat. PAC (Zetag 76)	med to high	$\sim 1.10^7$	2 g/kg TSS		~7,0	—	—	—	—	—	—	—	U/S	1	—	—	mg/l TSS	~3500	6,7	—	—	—	—	Dissolved air flotation	15
118	Phosphorus	COD/Nitrogen	Stabilization Pond effluent	Alum.	—	~630	80	6,9	5,5	—	—	—	—	—	—	—	U/S	U/S	U/S	U/S	mg/l total P	14,0 to 19,0	1,0 to 1,6	—	mg/l COD mg/l N	142-250 12-16	23,5-37 3,5-67	Settled jar test	46
119	Phosphorus	COD/Nitrogen	Stabilization Pond effluent	Alum.	—	~765	125	8,6	5,5	—	—	—	—	—	—	—	—	7,5/7,5	—	—	mg/l total P	1,5	0,05	—	mg/l COD & mg/l TKN	17,6 12,1	6,2 10,5	Settled jar test	16
120	Phosphorus	Various	Act. Sludge mixed liquor	Alum.	—	~630	145	12,5	5,8	—	—	—	—	—	—	—	—	—	—	—	mg/l P	7	2	—	mg/l COD	50	20	Activ. Sludge Pilot Plant	32
121	Phosphores	Various	Act. Sludge Effluent	Alum.	—	~630	315	27	6,0	—	—	—	—	—	—	—	—	—	—	—	mg/l P	17	0,62	—	U/S	—	—	Act. Sludge Settled	49
122	Phosphorus	Various	Raw Sewage	Alum.	—	~630	160	13,7	~6	Anionic PAC	10-20%	$>8.10^6$	0,8	—	—	—	U/S	U/S	U/S	20	U/S	U/S	U/S	(Overflow rate = 7,14 m/h				Settled jar test	3
123	Phosphorus	Various	Act. Sludge Effluent	Ferric Chloride	—	~162	78	12	~7	Nonionic Meyprofloc P3			0,5	—	—	—	U/S	~0,5	U/S	~0	mg/l P	4,5	<1	—	mg/l TOC mg/l ss	~18 ~50	6 4	Direct filtr. sand/anth.	27
124	Phosphorus	Various	Act. Sludge Effluent	Ferric Chloride	—	~162	176	27	8,8	—	—	—	—	—	—	—	U/S	~0,5	—	—	mg/l P	3,8	—	91	mg/l TOC	14	45±20	Sludge blank. Clarifier	28
125	Phosphorus	Various	Act. Sludge Effluent	Lime	—	—	250	—	? (~11,0)	Ferric Chloride	—	~162	4,2 as Fe	—	—	—	U/S	1	U/S	1/30	mg/l P	4,2	0,2	—	mg/l COD	62,4	37,4	Upflow Clarifier	18
126	COD	Various	Raw Sewage	Alum.	—	~630	80	5	U/S	—	—	—	—	—	—	—	U/S	0,5/10	—	—	mg/l COD	~700	—	58	—	—	—	Settled jar test (Imhoff cone)	50

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID(S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF.
				TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE		OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l^{-1}	ELEC. MOBILITY µm/s/V/cm	STREAM CURRENT µA	COLLOID CHGE. meq/l	PRIMARY COAGULANT		FLOCCULANT AID		UNITS	CONCENTRATION		REM. %	UNITS	CONCENTRATION			
							mg/l	as Me ion									G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN.		INITIAL	FINAL			INITIAL	FINAL		
127	COD	Various	Raw Sewage	Alum.	—	~630	546	47	5,9	—	—	—	—	—	—	—	400/25	1/30	—	—	mg/l COD	723	—	72	mg/l P mg/l N	31 82	97% 9%	Settled jar test	29
128	COD	Various	Raw Sewage	$FeCL_3$	—	~162	488	75	5,3	—	—	—	—	—	—	—	400/25	1/30	—	—	mg/l COD	723	—	72	mg/l P mg/l N	31 82	96% 9%	Settled jar test	29
129	COD	Various	Raw Sewage	$FeCL_3$	—	~162	60	9,22	9,0	—	—	—	—	—	—	—	U/S	0,5/10	—	—	mg/l COD	~700	—	70	—	—	—	Settled jar test (Imhoffcone)	50
130	COD	Various	Raw Sewage	Lime {$Ca(OH)_2$}	—	—	U/S	—	11,0	—	—	—	—	—	—	—	U/S	0,5/10	—	—	mg/l COD	~700	—	63	—	—	—	Settled jar test (Imhoffcone)	50
131	COD	Various	Raw Sewage	Lime {$Ca(OH)_2$}	—	—	520	—	11,0	—	—	—	—	—	—	—	400/25	1/30	—	—	mg/l COD	723	—	69	mg/l P mg/l N	31 62	94% 13%	Settled jar test	29
132	COD	Various	Raw Sewage	Lime {$Ca(OH)_2$}	—	—	350	—	11,0	—	—	—	—	—	—	—	U/S/50	0,2/24	—	—	mg/l COD	264	80	—	mg/l PO_4 mg/l SS	7,9 104	<0,2 25	Pilot Flocc. Sed system	25
133	Sludge Dewatering	—	Alum Water Treatment Sludge	Anionic (Betz 1120)	15 – 30	~5.10^6	12	—	—	—	—	—	—	—	—	—	U/S	1/1,5	—	—	sp. resist.: m/Kg. $.10^{-11}$	224	12	—	—	—	—	Sand Drying bed	39
134	Sludge Dewatering	—	Iron – Lime Sludge	Anionic (Betz 1120)	15 – 30	~5.10^6	6	—	—	—	—	—	—	—	—	—	U/S	1/1,5	—	—	sp. resist.: m/Kg. $.10^{-11}$	30	1,5	—	—	—	—	Sand Drying bed	39
135	Sludge Dewatering	—	Alum (Brown) Wat. Treat. Sludge	Cat. PAC (Magnafloc LT 24)	10%	>7.10^6	1,25	—	—	—	—	—	—	—	—	—	U/S	~0	—	—	Sludge Conc. %	0,25	12	—	—	—	—	Dissolved air flotation	12
136	Sludge Dewatering	—	Activated Sludge	Cat. PAC (Zetag 76)	med. to high	10-12. 10^7	4g/Kg	—	—	—	—	—	—	—	—	—	U/S	U/S	—	—	Sludge Conc. %	~0,4	15	—	—	—	—	Belt Press	15
137	$CaCO_3$ flocs	—	Lime Softening Wat. Treat.	Anionic (Nalcolyte 8174)		~3.10^6	0,05	—	10,0	—	—	—	—	—	—	—	U/S	U/S	U/S	U/S	Total Hardness	324	74	—	Filter run loss head	~35 hours ~2m	—	Sedimentation/ filtration	17
																						mg/l as $CaCO_3$							
138	MnO_2	—	Lab. prepared suspension	Ferric Sulphate	—	~562	25	5	7,0	—	—	—	—	−0,5	—	—	U/S	5/30	—	—	mg/l MnO_2	2,5	0,05	—	—	—	—	Settled jar test	42
139	MnO_2	—	Lab. prepared suspension	Alum.	—	~694	10	0,78	9,0	—	—	—	—	—	—	—	U/S	5/30	—	—	mg/l MnO_2	2,5	0,25	—	—	—	—	Settled jar test	42
140	MnO_2	—	Lab. prepared suspension	$CaCL_2$	—	~111	56	20	5,0	—	—	—	—	−0,9	—	—	U/S	5/30	—	—	mg/l MnO_2	2,5	0,15	—	—	—	—	Settled jar test	42

PRINCIPAL CONSTITUENT REQUIRING REMOVAL		OTHER CONSTITUENTS PRESENT	GENERAL DESCRIPTION OF WATER TYPE	PRIMARY COAGULANT						FLOCCULANT AID (S)				ELECTROKINETIC CHARACTERISTICS			MIXING CONDITIONS				REMOVAL PRINCIPAL CONSTITUENT				REMOVAL OTHER CONSTITUENTS			SOLID LIQUID SEPARATION FACILITY	REF
							DOSAGE										PRIMARY COAGULANT		FLOCCULANT AID			CONCENTRATION				CONCENTRATION			
				TYPE	CHARGE DENSITY	MOL WT.	mg/l	as Me ion	OPT. pH	TYPE	CHARGE DENSITY	MOL. WT.	DOSAGE mg l^{-1}	ELEC. MOBILITY μ A/v/cm	STREAM. CURRENT μ A	COLLOID CHGE. meq/ l	G s^{-1}	TIME MIN.	G s^{-1}	TIME MIN.	UNITS	INITIAL	FINAL	REM. %	UNITS	INITIAL	FINAL		
141	MnO_2	—	Lab. Prepared suspension	Cat. PDADMAC		$>5.10^4$	0,25	—	5,0	—	—	—	—	—	—	—	U/S	5/30	—	—	mg / l MnO_2	2,5	0,25	—	—	—	—	Settled jar test	42
42	$MgCO_3$	SiO_2	Lab. Prepared suspension	Anionic (BTI-A-130)		$>10^6$	1	—	>11,0	Polyelectrolyte degraded by high shear stirring for 2 hours to limit enmesh-ment of SiO_2 thereby providing separation of $MgCO_3$ and SiO_2							U/S	U/S	—	—	mg / l $MgCO_3$ % ABS	5000 >40	— ~20	— —	mg / l SiO_2	5000	—	Settled jar test	55
143	Disperse dyes (1,4 - bis (Methylamine) anthraquinone and p - nitroaniline → 2 - 2' (m-tolyimi no) diethanol + dispersing agents		Textile dyeing Wastewater	Alum	—	~630	~25	2	5,0	Cat. PEI (Dow-PEI 400)		$\sim 6.10^4$	5	—	—	—	U/S	10	U/S	10	mg/l dye	100	5	95	—	—	—	Settled jar test	26
144	Colour compounds (lignin degradation products)		Kraft Mill Caustic Extraction effluent	$ALCL_3$	—	~241	193	22	5,0	—	—	—	—	—	—	—	U/S	5/10	—	—	APHA Colour units	950	—	98	—	—	—	Filtered jar test	38
145	Colour compounds (lignin degradation products)		Kraft Mill *Caustic Extraction* effluent	$FeCL_3$	—	~270	216	45	3,2	—	—	—	—	—	—	—	U/S	5/10	—	—	APHA *Colour* units	880	—	93	—	—	—	Filtered jar test	38
146	Organic Solids and COD	Various	Tanner unhairing effluent	$Na(PO_3)_6$	—	—	20	—	12,5	Anionic *PFA-10* Cationic PFC-3			3 0,5	—	—	—	U/S	5/5	U/S	5/10	mg/l SS	$\sim 14.10^3$	180	99	mg/l COD	$\sim 90.10^3$	56%	*Settled jar test*	21
147	Heavy metals (Fe+Zn+Cu+Mn+Pb)	Sulphates	Base metal *mine* drainage	U/S Anionic? Poly.	4	9.10^6	0,7	—	9,5	—	—	—	—	—	—	—	U/S	0,75/15	—	—	mg / l Me	326	0,1	—	mg/l SO_4	1195	—	Settled "jar test"	24

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A.4 WATER TREATMENT PLANT WASTE SLUDGE DISPOSAL

A.4.1 General

Water treatment plant wastes originate from two sources: the clarifier underflow and the filter backwash or washwater recovery process. Characteristics of the wastes produced depend very much on the type of raw water and the coagulants, flocculant aids, etc., used. In general, waste sludge from water treatment plants may be described as a non-Newtonian, bulky, gelatinous substance typically comprising metal hydroxide and inorganic/organic material removed from the treated water. Such sludges generally have a low solids concentration of the order 2000 to 15000 mg l^{-1}. BOD values are typically of the order 30 to 100 mg l^{-} with COD values of the order 500 to 10000 mg l^{-1}.

In general, water treatment plant sludges are of a concentration too low for convenient handling and/or landfill (a 20 per cent total solids concentration being minimal); compressible so that dewatering is hampered and of such a composition that direct disposal on land gives rise to soil clogging.

Particularly problematical are sludges produced from water treatment plants using aluminium sulphate as coagulant. Lime sludges from plants practicing softening operations are generally easier to dewater. Ferric sludges have properties intermediate between the two.

The advantage of sludge dewatering prior to final disposal is that the volume of sludge is greatly reduced and handling properties improved. The following sections briefly describe methods of dewatering water treatment plant wastes giving, where possible, inherent advantages and disadvantages and in general terms, conditions of operatio

A.4.2 Disposal to Watercourses

Direct discharges of water treatment plant wastes to surface waters is obviously the most economical solution in terms of treatment costs. However, these wastes present a considerable pollution source and, although many plants continue with such a practice, alternative means of disposal are usually sought. In some cases it may be feasible to discharge filter backwash water to watercourses although this too in many cases is beyond the handling capacity of natural streams.

A.4.3 Disposal to Municipal Sewers

A solution to the water treatment sludge problem in many cases is to discharge the waste stream into sanitary sewers and thereby effectively treat the sludge at the waste water treatment plant. With such a practice care must be taken that optimum pH conditions for biological efficiency are maintained. Apart from this, however, there does not appear to be much evidence indicating a detrimental effect on biological activity. For plants with primary sedimentation the presence of a coagulated sludge may well result in decreased loads to the subsequent biological processes(17). It has been reported(16) that the discharge of water softening lime sludges to municipal sewers may remove 45 per cent of the BOD and 75 per cent of suspended solids during primary (upflow) sedimentation. The combined sewage-lime sludge may subsequently be dewatered by processes such as vacuum filtration. It has been stated that although alum sludge is beneficial during raw sewage primary sedimentation, this is especially so if flocculation of the combined streams occurs before sedimentation.

When considering direct discharge to a sewer, the following considerations have been recommended(8, 19):

(a) Amenability of the waste sludge to existing treatment processes;

(b) Hydraulic capacity of sewage treatment facilities;

(c) The effect of the waste on the final plant effluent;

(d) Cross connections must be precluded, possibly by a water break, to ensure that if the sewer backs up the raw sewage passes elsewhere;

(e) Water treatment sludge should be discharged on a continuous basis rather than as a slug flow;

(f) The discharge of gelatinous metal hydroxide sludges may choke trickling filters, if this is the treatment process used;

(g) Possibility of silting and plugging of pipelines. One example has quoted a minimum flow velocity of 0,75 m s^{-1}(14).

In cases where the wastewater plant is large compared to the water treatment plant, discharge to sewers may offer a satisfactory solution, provided that sludge handling facilities at the wastewater plant are adequate to cope with the greater sludge volume. Lime sludges may preclude such a method of disposal since deposition problems may be overwhelming and settling problems in the wastewater plant, for example in anaerobic digestors, may be serious.

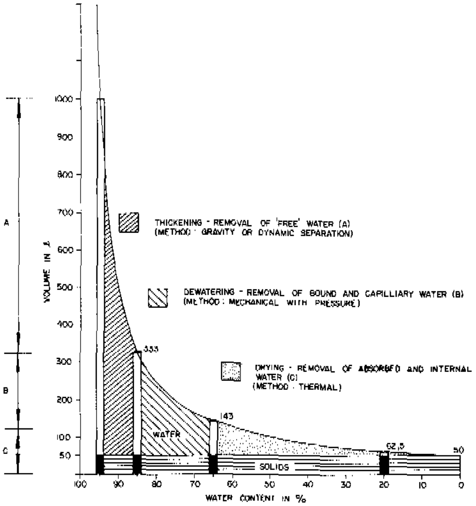

FIGURE A.4.1: Reduction in Sludge Volume at Various Stages of Water Removal. (Assumed 1 m^3 of sludge at 95% Moisture from Solid/Liquid Separation Facility).

A.4.4 Thickening

Thickening waste sludges prior to costly dewatering processes is often a very important step in the overall disposal scheme. The volume of sludge to be subsequently dewatered is markedly reduced. Figure A.4.1 is a conceptual presentation of the volume decrease during thickening compared to that by dewatering operations. (Note that water treatment plant sludges, after solid/liquid separation, are usually much less than the 5% starting concentration shown in Figure A.4.1).

Gravity thickening, although quite widely practiced, is relatively limited with water treatment plant sludges. In general, a maximum of 3% thickened sludge concentration may be expected(7, 12). The use of polyelectrolytes as sludge conditioners may slightly increase the final concentration attained. Kos(13) recommends a solids loading rate of 15 to 24 kg m^{-2} h^{-1} with a depth of tank 2,4m (1,5m thickening zone) for alum sludge with powdered activated carbon and a thickened concentration of 2,5 to 3,0 per cent.

More attractive in terms of thickening efficiency is flotation thickening. A disadvantage is that in some cases satisfactory solids recovery may not be possible without, say, polyelectrolyte conditioning. However, the much higher final concentration together with the much diminished thickener unit size is probably more than compensatory. For example, Bratby and Marais(4) applied dissolved air flotation to thicken the sludge from a water treatment plant treating brown humic coloured waters (coagulants used during treatment of the raw water were 10 mg l^{-1} sodium aluminate followed by lime to adjust the pH to 5,5 after subsequent addition of 50 mg l^{-1} aluminium sulphate). Because of the gelatinous nature of the sludge, the concentration at the bottom of the settling tanks never exceeded approximately 2500 mg l^{-1} (0,25%). By applying flotation thickening to the settled sludge (in conjunction with a cationic polyelectrolyte at a dosage of 0,5 g kg^{-1}) float solids concentrations of up to 12% were achieved by flotation. That is, the waste sludge volume could be reduced by a factor of 0,02, or one-fiftieth. It was pointed out that the increased chemical cost required for polyelectrolyte addition would constitute a mere increase of 1,43% of the existing overall running (chemical) costs.

A.4.5 Dewatering

Dewatering is the stage in the overall disposal strategy where the waste sludge is rendered in a handleable form for mechanical moving and trucking to ultimate disposal sites or in a form suitable for further drying. The several existing dewatering systems will be discussed briefly in the following sections. Also included (although perhaps not strictly dewatering operations as such) are coagulant recovery processes.

A.4.5.1 Vacuum Filtration

Rotary vacuum filters provide a continuous process dependent on a filtering pressure of less than 1 atmosphere. The vacuum is applied by a dry vacuum pump on the downstream side of the filter septum (see Figure A.4.2). The filter medium is either a rotary fabric belt which is continuously and automatically washed or a series of overlapping coils. Operation passes through three zones: firstly a pick-up or form section where a vacuum is applied to draw liquid through the filter media and to form a covering of partially dewatered sludge. Suction is maintained through the cake drying zone to continue the dewatering. After the final zone, a concentrated sludge cake is discharged.

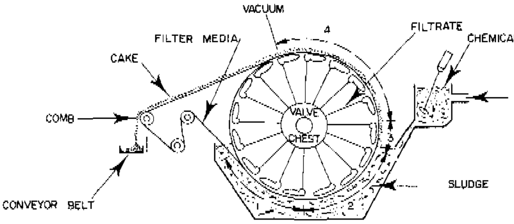

FIGURE A.4.2: Cake Processing Phases for Rotary Vacuum Filte

A large number of factors affect the actual yield from a vacuum filter such as depth of submergence, speed of rotation, solids content and filterability of the sludge. A large variety of sizes are available ranging from 0,9 to 3,6m diameter and 0,3 to 0,6m in length giving filter areas of from 1 to 75 m^2.

Lime sludges dewater successfully with vacuum filtration although the coil types are subject to incrustation of the coils. Belt type filters yield a crumbly cake of about 65% solids (30% solids feed) which is sufficiently dry for landfill or road stabilization.

With alum sludges (at about 1,5% solids feed) solids appear to penetrate the fabric readily and a solution in many cases is to use some form of precoat, for example, diatomaceous earth. The precoat is applied to the drum of the rotary vacuum filter to a depth of about 5 cm(12) before alum sludge filtration. Cake solids with alum (precoat) filtration range from 20 to 30 per cent. Precoat requirements range from 30 per cent for concentrated sludges (-5 per cent) to 50 per cent for dilute sludges (< 1 per cent). Filtration rates with alum sludges are of the order 0,1 to 0,2$m^3m^{-2}h^{-1}$. The filtrate solids are of the order 10 to 15 mg/l. A disadvantage of precoat operation is that associated running costs may be excessive. An alternative is polymer preconditioning. However, in some cases the applied dosage is very critical(15) and may give rise to operational problems.

Although favourable results have been reported for dewatering of lime sludges, this is not always the case, especially where high magnesium concentrations are present which may result in dewatering characteristics similar to those of alum sludges. Furthermore, since dewatering of dilute sludges (i.e. without prior thickening) is precluded with vacuum filtration, in some cases vacuum filtration of alum sludges may be economically and technologically unfeasible and other methods may be preferable.

A.4.5.2 Centrifugation

Centrifugation may be employed as a single process (without a thickening stage) to produce a product for final disposal, or it can be employed as a "thickening" device to prepare the waste for additional dewatering. Advantages of centrifugation are the small space requirements, complete process automation and ability to handle dilute (settled) or thickened sludges.

A further advantage of centrifugation over filtration is in cases where recalcination of lime sludges is required. In cases where magnesium hydroxide is present in the sludge (the presence of which, continuously recycled with the reclaimed lime, would give rise to build-up of impurities in the system) it is possible to operate the centrifuge such that magnesium hydroxide flocs are separated from the sludge and discharged with the centrate. However, although successful for lime sludges, in some cases centrifugation may not be suitable for alum sludges since final concentrations of 15 to 17 per cent only are usually attainable(1).

Two types of centrifuges which have been most reported as applied to water treatment plant sludges are the solid bowl scroll and basket types.

The scroll centrifuge is basically a rotating cylindrical bowl with a conical end to allow solids discharge. The opposite end of the bowl has effluent ports of varying distance from the imperforate bowl wall, thus allowing different "pond depths" for liquid discharge. Inside the imperforate bowl is a screw conveyor that rotates at a slight differential speed relative to the bowl. This screw conveyor moves the thickened solids to the conical end of the bowl for discharge from the centrifuge.

For alum sludges conditioned with polyelectrolytes a very short sedimentation time in the centrifuge (less than 1 minute) is required for solids thickening. With influent solids concentrations of approximately 3 per cent, the scroll centrifuge may be expected to produce a cake discharge of 24 to 28 per cent with polyelectrolyte conditioning(12) (of the order 1,5 g kg^{-1}). With filter backwash waters (1 to 2 per cent solids) cake discharges of 18 per cent have been reported(12).

A disadvantage reported with the scroll centrifuge is the high centrate solids concentration-approximately 500 mg l^{-1} (12).

Variables influencing solids recovery and cake concentration with the scroll centrifuge are the centrifugal acceleration produced by the bowl's rotational speed, the shape of the bowl, the pond depth, the pitch of the screw conveyor and the differential speed between screw conveyor and bowl.

The basket, or imperforate bowl knife centrifuge (see Figure A.4.3) uses a vertical solid bowl and is said to induce less shear to flocculated solids. Thickened sludges are removed at periodic intervals, completely automatically.

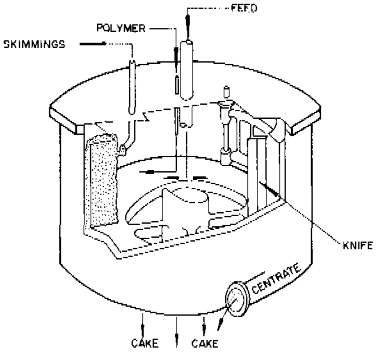

FIGURE A.4.3: Schematic Diagram of a Basket Centrifuge

With the basket centrifuge applied to alum sludges of 1 to 1,5 per cent solids, cake concentrations of 11 per cent have been reported(12) without prior conditioning. With polyelectrolyte conditioning, cake solids of 15 per cent have been reported(15) with a cycle time of approximately 20 minutes. A disadvantage of the basket type is the low solids loading necessary to achieve a suitable (handleable) cake of about 15%. However, the centrate is generally of a higher quality than the scroll type.

A.4.5.3 Pressure Filtration

Pressure filtration is essentially a batch process in which preconditioned sludge is pumped into cloth lined spaces retained between a series of substantial plates (See Figure A.4.4). Sludge is introduced through holes in the centre of the plates into the space between the filter cloths at a pressure of 400-650 kPa. Filtrate is forced through the cloths and the retained solids form a cake approximately 25-35mm thick. Pressing time varies considerably with sludge character, from 3 hours to 3 days in the usual range. Discharge of the pressed cake can be manually or automatically controlled by releasing pressure and separating the plates.

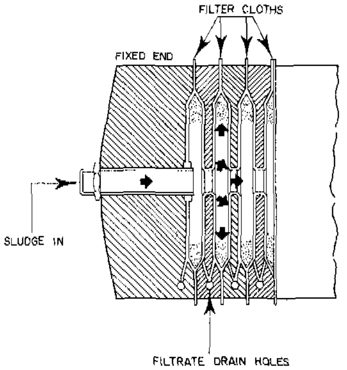

FIGURE A.4.4: Cutaway View of a Filter Press

Press plates used to be made of cast iron, which often gave rise to problems with cracking due to unequal feed distribution but these have largely been superseded by grp, polypropylene or moulded rubber units.

Filter presses have the advantage that higher pressures may be applied for dewatering; 5000 to 20000 G. Practicable centrifugal pressures are of the order 1000 G.

With polyelectrolyte conditioning and after thickening to 1,5 to 2 per cent solids, filter cake concentrations of 15 to 20 per cent solids are attainable with alum sludges(2). At times a diatomaceous earth precoat of, say, 0,25 to 0,4 kg m^{-2} of filter area may be beneficial to facilitate discharge of the cake and prevent binding of filter material(15).

With lime conditioning of alum sludges filter cake concentrations of 40 to 50 per cent solids are obtainable(12). Lime requirements in such cases may amount to 25 per cent of the waste sludge (m/m). Typical cycle times are of the order 90 to 120 minutes but depend very much on the sludge conditions.

Two disadvantages have often been associated with filter presses: the first is the short life of the filter cloths and the second the lack of automation. However, modern synthetic fibres greatly extend cloth life and increased use is made of automatic feeding and pressing cycles. It is only at the end of the pressing cycle that no fully automatic process for discharging the sludge cake has as yet been used.

Pressure filters have often been the dewatering facility chosen due not only to the high cake solids concentrations attainable but also the lower general operating costs.

A.4.5.4 Belt Filter Press

The belt filter press has been under development for about 20 years and many variations have been evolved by machinery suppliers. In essence, they all consist of a horizontal perforated or woven belt on which the conditioned sludge is fed and a press belt which bears on the other; the belt being kept in contact by a series of individually adjustable rollers (see Figure A.4.5). Dewatering is carried out in three separate stages: An initial draining zone followed by a press zone and finally a shear zone. In the press zone, the sludge is subjected to mechanical pressure between press belt and filter belt. The belt speed is infinitely variable as is the compression of the rollers enabling the belt press to be easily adjusted to suit various sludges of differing dewatering characteristics.

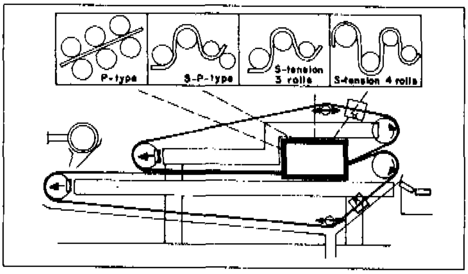

FIGURE A.4.5: Filter Belt Press. (Courtesy Envirotech).

Using alum sludges (of approximately 2,5 per cent feed concentration) preconditioned with 5 to 7 g kg^{-1} (m/m) polyelectrolyte, filter cake concentrations of 8 to 12 per cent have been reported$^{(12, 20)}$ with filtrate concentrations of 25 to 60 mg l^{-1}.

A.4.5.5 Sludge Concentrator "Rotoplug" Type

This concentrator consists of two main units operating in series (see Figure A.4.6). The first unit is a rotating horizontal cylinder whose outer surface is covered with a fine nylon fabric of special weave which allows interstitial water to drain away by gravity from the rotating plug of sludge. The rotation of the cylinder causes the deposit to form into a rolling mass which further dewaters the primary deposit through the action of its own weight. Distention of the rolling mass in an axial direction causes the end portion to be cut away by the end flanges and dropped to a secondary compression filter.

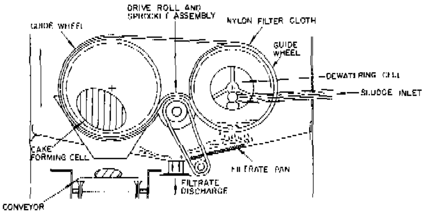

FIGURE A.4.6: Rotating Gravity Concentrator

Cake solids concentrations achieved with this system appear to be of the following orders$^{(18)}$: alum sludge: 12 per cent with polyelectrolyte conditioning; ferric chloride sludge: 20 percent with polyelectrolyte conditioning; calcium carbonate (lime) sludge: 47 per cent (polyelectrolyte conditioning) and calcium carbonate-magnesium hydroxide sludge (hot-lime): 17 per cent.

A.4.5.6 Thermal Conditioning

Heat treatment of sludge under pressure (175 to 200°C at 1200 to 1400 kPa) results in the breakdown of the gelatinous flocs of alum sludges and an increased rate of dewatering.

An example is the Porteous process developed over 45 years ago. It is a batch process which, although originally beset by many operational difficulties, has been developed into a process operationally reliable and economically viable.

A further example (principally used in wastewater treatment sludge conditioning) is the Zimpro process of wet oxidation. This process differs from the Porteous process in that air is introduced into the pressure vessel. Disadvantages with both these heat treatment processes in the area of wastewater treatment have been the presence of a strong pervading smell-although with water treatment sludges this may not be a problem; the considerable energy input to achieve the necessary temperatures and that maintenance requirements of pumps and the "shell and tube" heat exchangers are high and represent a significant operating cost.

A.4.5.7 Freezing

The freeze treatment process gives rise to dehydration of sludge particles by freezing the water closely associated with them. As the sludge is chilled the particles are first concentrated by selective freezing of the liquid phase and finally dehydrated as the total mass is frozen. On thawing, water which has left the sludge matrix to form ice crystals has little tendency to return to the sludge particles. Coarse "coffee ground" solids thereby remain which thicken readily and are easily filtered. Gravity thickening of alum sludges after freeze treatment results in solids concentrations of the order 20%(compared with approximately 2% before freezing). With vacuum filtration of the thickened solids cake concentrations of 30% are attainable(21). As an alternative to vacuum filtration, direct discharge to lagoons has been reported to result in solids concentrations of 60 to 70 per cent(3).

The freezing process is carried out in batch mode to ensure complete freezing (it has been reported (21) that even if only 10 to 20 per cent unfrozen particles remain, the beneficial effect of freeze treatment is largely eliminated). Freeze treatment normally requires a pre-thickening step to provide a uniform feed concentration of the order 2 to 4 per cent solids. The objective of pre-thickening is to reduce the volume of sludge to be frozen. The cost of conditioners required for pre-thickening is usually offset by the savings in cost during freezing.

Although post-thickening may be practiced, the ready dewatering capability of freeze-treated sludge makes direct discharge to lagoons or drying beds feasible.

The practicable and economical temperature range for freeze treatment is from -15°C to -4°C. Within this temperature range, adequate freeze treatment is provided at a 20 to 60 minute freezing time. In naturally colder climates, natural freezing could be used during winter months to minimise operating costs.

The greatest advantage of freeze treatment is its ability to treat effectively any quality of sludge. Freeze treatment is a volumetric treatment system that is insensitive to variations in sludge quality and never requires any kind of chemical treatment(21) - apart from that required for the pre-thickening stage. A dramatic example of the efficacy of freeze treatment is the Søndersø Treatment plant of Copenhagen, Denmark(2, 8). Natural freezing takes place in lagoons 1 m deep with a draining gravel bottom. As a result of freezing and thawing cycles and drainage, the amount of sludge remaining in the lagoon after 2 years of operation was only 4 cm.

The obvious disadvantage is the power cost. However, with the marked dewatering ability of freeze-thawed sludge, overall costs may be competitive; Furthermore, in colder climes natural aided freezing will probably diminish significantly operating costs.

A.4.5.8 Coagulant Recovery

A process incorporating recovery of coagulant for reuse may be feasible in terms of minimising sludge disposal costs. In the case of alum sludges, the recovery process is accomplished essentially in three steps:

Firstly, thickening of the waste sludge is almost a prerequisite to minimise volumes and to ensure a sufficiently high concentration of recovered alum (at least 2 per cent) (10). Secondly, the thickened sludge is acidified with sulphuric acid to produce aluminium sulphate. Acid, in excess of that for reaction with aluminium is required to ensure a low pH (-2,0). Low pH values improve the settling and filtering characteristics of the solid matter that must be removed to produce an alum solution suitable for reuse. Thirdly, undesirable suspended matter remaining is separated from the alum solution. Such separation may be accomplished either by settling out the solids in a basin or by removing the solids with a filter press. In settling, the recovered alum is the overflow and the solid residue is removed from the basin via the underflow. The underflow solids are usually mixed with lime for pH neutralization and conditioning prior to dewatering by vacuum filtration, pressure filtration and so on. In some cases the underflow is passed directly to a dewatering facility. This has the advantage of improving the percentage of recovered alum and reducing the subsequent lime dosage necessary to neutralise the waste sludge prior to disposal. With this procedure cake solid concentrations, using pressure filtration, have been reported to be of the order 40 to 55 per cent(5). The recovery of reusable alum is of the order 50 to 75 per cent(20) with an acidulator retention time of 10 to 25 minutes. The stoichiometric amount of sulphuric acid required is 1,9 kg H_2SO_4 per kg $Al(OH)_3$. An excess is usually required of the order 8 per cent of the stoichiometric requirement.

Advantages of acid treatment are that acidified sludge dewaters at a faster rate(12) (since aluminium hydroxide has been dissolved) and the final volume for disposal is lower due to removal of the aluminium hydroxide fraction(15). However, the alum recovery process is not widely used principally because of the relatively poor efficiency of recovery(5) and the progressively poorer quality of alum recovered. Furthermore, excessive build-up of acid soluble impurities may occur: for example, if present, organic colour compounds, iron, manganese and so on.

As an example(10), if the alum feed to the raw water is 30 mg l^{-1} and the raw water contains 0,05 mg l^{-1} iron and recovered alum is 3 per cent, iron would be concentrated 1000 times in the recycle, i.e. to a concentration of 50 mg l^{-1}. With progressive accumulation, in twenty days time after commencement of alum recycling, iron would be 1000 mg l^{-1} in the recycle and 1,0 mg l^{-1} in the final water.

An operational problem noted during acidic alum recovery processes is the generation of gas bubbles (probably CO_2) which serves to impede subsequent gravity thickening(1) and develop a troublesome froth layer on the surface of the thickener (20).

Although in some cases acid alum recovery and recycling within the water treatment plant may not be feasible for instances where impurity build-up is likely, the process may be economical where reuse of recovered alum at a wastewater treatment plant for phosphorus precipitation(6) is feasible. In this case the presence of impurities in the recovered alum is probably not a disadvantage(11). Advantages would be, apart from phosphorus precipitation, improved COD and solid removals during primary sedimentation. However, the wastewater treatment plant must have sufficient capacity to handle the increased solids load.

In some cases, where the cost of recovered alum is higher than the cost of virgin alum itself, the advantages of improved sludge dewatering characteristics may not compensate the cost of acid treatment. Furthermore, in many plants the degree of skilled operator control required for the process may preclude consideration; Other less operator intensive processes may be more viable.

A further recovery process of importance for water softening plants is lime recalcination. Essentially the lime recovery process comprises the following steps(2): Sludge thickening and/or blending (in some cases recarbonation is utilised in this step); Dewatering by centrifuge or vacuum filter; Flash drying of dewatered sludge by use of off-gases; recalcining at high temperature, i.e. converting calcium carbonate to calcium oxide; Product cooling, where required.

The two predominant types of recalciners are the rotary kiln and fluidised bed furnaces. Fluidized bed furnaces appear to have gained favour; the system operates more economically, produces less dust, produces a harder CaO product, is less susceptible to air-slaking, requires less installation space and is capable of faster start-up and shutdown. Other types are variations of muliple-hearth furnaces.

Successful recalcination relies on the production of an end product of minimal impurities. For example the concentration of magnesium should not exceed 10 per cent. Because of this limitation, many water treatment sludges are not amenable to recalcination. However, in cases where recalcination is feasible, several plants show a definite profit(2); the quantity of lime reclaimed may in some cases exceed that required for originally softening the water.

A typical recovery process(2) includes thickening of the calcium carbonate sludge to 20 to 30 per cent solids; dewatering by centrifuge to about 67 per cent solids; calcination at temperatures of 1000 to 1200°C in an oil fired rotary kiln.

Separation of magnesium from the sludge prior to recalcination may in some cases be accomplished at the dewatering (centrifugation) stage by suitably adjusting the centrifuge operating conditions. Recovery of $Mg(OH)_2$ may lead to a useful end product; Carbonation of softening sludge produces $MgCO_3$ (which can be physically separated from $CaCO_3$ precipitates), which may be reused as a water treatment coagulant in place of alum in certain cases (9). When tastes, odours or colour are present in the raw water, the centrate is usually wasted rather than recycled to the plant. The effect of silt and clay particles, if present in excessive amounts, may give rise to a recalcined product with the characteristics of cement rather than lime.

In certain cases removal of such particulate material prior to softening operations may be a solution.

A useful end product of the recalcining process is the production of CO_2 which is present in the furnace stack gas (15 to 27 per cent CO_2). The CO_2 liberated from $CaCO_3$ on reduction to CaO may be used for recarbonation during water conditioning in the plant or it may be recovered and marketed as "liquid or dry ice".

A.4.5.9 Lagooning

Lagooning has been one of the most popular methods of sludge treatment due to its simplicity and low cost of operation; In areas where ample land is available, lagooning is quite economical.

The general procedure in constructing a lagoon is to enclose a suitable area with dikes or excavation. Normally no attempt is made to provide additional underdrainage although artificial drainage would appear to present significant advantages(8). The method of operation is to fill the lagoon with sludge and allow it to dry whereupon more sludge is added and the process repeated until the lagoon is full of sludge dry enough for removal.

Lagooning of alum sludges may not produce a handleable end product - at times typical concentrations range from 1,5 to 2 per cent at the surface to of the order 10% at the bottom(1) with average concentrations of the order 4 to 5 per cent. Such sludges would require further dewatering for landfill purposes. However, in colder climates, natural freezing and thawing may improve conditions, especially if there are provisions for drainage, with reported concentrations of the order 18 per cent(1).

With lime sludges lagooning may yield final concentrations of 50 per cent or more.

Problems may exist with lagoons due to insect breeding and danger to children if situated in proximity to inhabited areas. Fencing may in such cases be a necessity.

A.4.5.10 Drying Beds

Sand drying beds, in cases where suitable land areas are available, are used extensively for dewatering sludges. Typically they are constructed by placing a 15 to 25 cm layer of sand (-0,5 mm ES) over an underdrainage system consisting of 30 cm of 3 to 6 mm graded gravel laid over drain tiles or 15 to 20 cm drain pipes. Considerations in sand bed drying include the underdrainage system design; sand type with void ratio, permeability, porosity, uniformity coefficient, depth, replacement sand and so on; bed loading; clogging; distribution method; and supernatant collection(9). Other parameters include air temperature and humidity; wind velocity; and viscosity of the sludge.

An alternative to sand beds is wedge wire filtration which utilises mesh sizes ranging from 0,125 to 0,25 mm. With a 2 per cent alum sludge concentration a typical sludge depth is 15 to 30 cm. Such beds are usually left covered for the first 7 to 10 days and then left open for a 21 day draining and drying period. Further layers of sludge may then be placed over the old(2). Such beds are normally constructed in pairs with a travelling cover.

Disadvantages of drying beds are the poor dewatering obtained in cold or rainy climates; high labour costs for collection of dried sludge and hauling to disposal sites and the long times required for adequate dewatering.

Application of alum sludges to depths 0,6 to 1,0 m deep requires drying times sometimes in excess of 4 to 6 months before the sludge attains a concentration of, say, 20 per cent and may be used for landfill. With lime sludges, a 1,5 m layer should dry to a 50% solids concentration after about 4 months. However, in the choice between lagoons and drying beds, especially in cases where land costs are high, drying beds would appear to offer a more feasible solution. The inclusion of underdrains and a sand layer should not greatly add to the overall costs and dewatering should be accelerated.

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Here is an outline of "Coagulation and Flocculation"

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Stability and Destabilization; Definitions; Performance Criteria; Summary

2 Colloids and Interfaces
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3 Coagulants
Commonly Used Metal Coagualnts; Chemistry of Metal Coagulants; Natural Polyelectrolytes; Structure and Characteristics of Synthetic Polyelectrolytes

4 Destabilization with Metal Coagulants
Destabilization of Hydrophobic Colloids; Extent of Hydrolysis and Adsorption; Effect of Coagulant Dosage; Effect of Colloid Concentration; Effect of pH; Destabilization of Hydrophilic Colloids; Organic Colour Removal; Virus Removal; Effect of Anions; Phosphorus Removal in Wastewater Treatment

5 Destabilization with Polyelectrolytes
Mechanisms of Destabilization; The Bridging Mechanism; The Electrostatic Patch Mechanism; Turbidity Removal; Organic Colour Removal; Removal of Microorganisms; Polyelectrolytes as Flocculant Aids; Polyelectrolytes as Sludge Conditioners

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