Pollution prevention strategy at an H-acid manufacturing unit

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Abstract

H-acid is a dye intermediate. In India, it is mainly manufactured by small and medium-sized enterprises (SMEs) with a production capacity of between ten and 100 tonnes per month. The promotion of various types of employment-generating SMEs in India has resulted in multi-media pollution problems. Through the implementation of simple pollution prevention measures, substantial cost savings can be obtained in an H-acid manufacturing unit. For example, process modification can increase product yield as well as reducing the COD load to wastewater treatment systems.

Résumé

L'acide H est un composant de colorants. En Inde, il est principalement produit par les petites et moyennes entreprises (PME) dont la capacité de production varie entre 10 et 100 tonnes par mois. Le développement de différents types de PME indiennes génératrices d'emplois a entraîné de problèmes de pollution « multimédias ». L'application de mesures simples de prévention de la pollution permettrait une réduction significative des coûts au sein d'une unité de production d'acide H. Ainsi, une modification du processus de fabrication peut accroître le rendement du produit tout en réduisant la charge DCO qui parvient aux systèmes de traitement des eaux usées.

Resumen

El ácido H es un tinte intermedio. En la India se manufactura principalmente en pequeñas y medianas empresas (PYMEs) con una capacidad de producción entre 10 y100 toneladas al mes. La promoción de diversos tipos de PYMEs generadoras de empleo en la India ha resultado en problemas de contaminación en distintos medios. Mediante la puesta en práctica de simples medidas de prevención de la contaminación se pueden obtener sustanciales ahorros en los costes en una unidad de manufactura de ácido H. Por ejemplo, la modificación del proceso puede aumentar el rendimiento y reducir la carga de COD en los sistemas de tratamiento de aguas residuales.

H-acid (1-Amino, 8-Naphthol, 3-6 disulphonic acid) is one of the dye intermediates used in the manufacture of acid, reactive and direct dyes. It is manufactured mostly by small and medium-sized enterprises (SMEs) with a production capacity of 10-100 tonnes per month (TPM). In India, SMEs are considered as employment generators. Consequently they are usually built on the fiscal regime of incentives, subsidies and tax concessions with little attention paid to productivity and resource conservation. On the other hand, promotion of these units has created multi-media pollution problems.

Due to the gradual abandonment of manufacture of toxic dye intermediates in the developed countries, most of these SMEs turned out to be potential foreign exchange earners. This trend calls for establishing the peaceful coexistence of environmental protection and economic development in this sector.

This article concerns the considerable savings (US$ 60,000 per year) that can result from the implementation of simple pollution prevention measures in a typical 10 TPM H-acid manufacturing unit. Through process modification the product yield is increased by 7.7 per cent, resulting in the elimination of about 40 per cent COD load to the subsequent wastewater treatment system. Potential areas for hazardous waste minimization and exchange are also highlighted.

Introduction

The dyestuff industry in India made remarkable progress during the 1960s and 1970s. There are at present over 1000 units in the small-scale sector engaged in the manufacture of dyes and intermediates. Most of these units are located in the western part of India, i.e. the States of Gujarat and Maharashtra.

H-acid (1-Amino, 8-Naphthol, 3-6 disulphonic acid) is one of the dye intermediates used in the manufacture of acid, reactive and direct dyes. The unit discussed in this article is located in the Odhav industrial estate of Ahmedabad district, in the northwestern region of India.

Due to the usage of high-strength acids and alkalies in the manufacture of H-acid, the combined wastewater stream was contaminated with high chloride and sulphate content. In addition, the presence of toxic naphthalene-based dye intermediates in the wastewater made it non-biodegradable.

In order to meet the existing terminal standards, these industries have to install capital-intensive and more sophisticated treatment systems, with heavy recurring costs. Therefore, the feasible alternative was to implement various pollution prevention measures using a "methods approach", with the objective of not only optimizing chemical usage but also reducing the pollution load to the subsequent wastewater treatment system.

Manufacturing process and waste generation

H-acid production was a batch process. On average, 30-34 batches were carried out in a month. Naphthalene was the starting material for H-acid synthesis. It was subjected to a series of chemical reactions like sulphonation, nitration followed by neutralization, reduction, fusion and isolation. The H-acid slurry after isolation with sulphuric acid was filtered in a Neutch filter, centrifuged, dried and packed. A schematic production process indicating the sources of pollution is shown in **Figure 1**.

Based on the wastewater survey conducted at this unit, the "pollution inventory data" presented in **Table 1** were evolved.

All the above mentioned discharges were batchwise. In order to simulate the characteristics of combined factory discharge which would serve as a design basis for the subsequent wastewater treatment system, a volume-proportionate sample designated as "factory composite" was prepared in NPC's laboratory.

Based on the above data, and by studying the various unit processes and operations involved in the H-acid production, the following in-plant pollution prevention measures were recommended.

In-plant pollution prevention measures

Process modification

Yield improvisation by the installation of an additional autoclave: around 700 kg of amino solution was produced per batch. Out of this, only 550 kg amino solution per batch was processed in the autoclave (2000 litre capacity). Since the unit had only one autoclave, the remaining 150 kg of amino solution per batch was accumulated for five batches and collected in a wooden vat (7000 litre capacity) and processed in Koch acid route.

The frequency of amino solution processed in the Koch acid route was five batches per month.

Figure 1
Production process and sources of pollution[1]

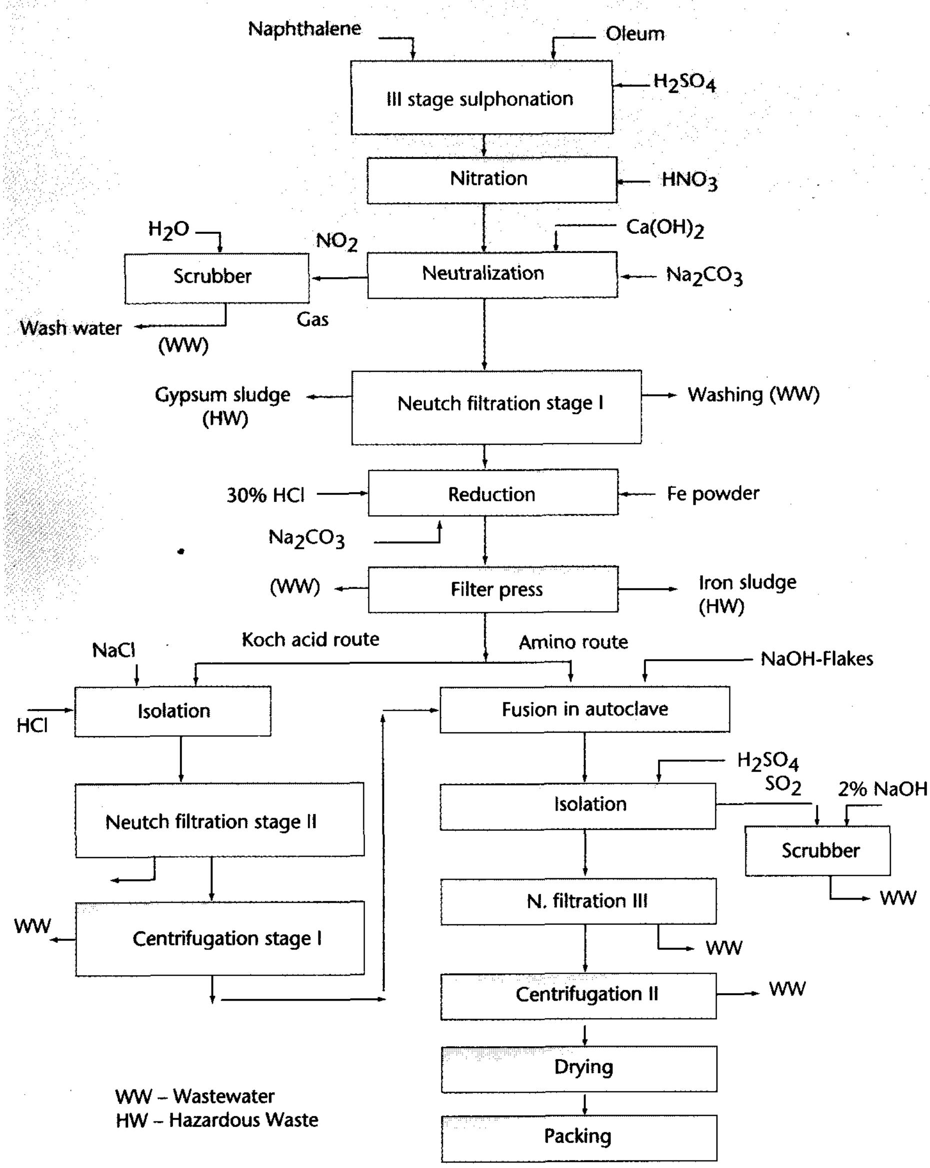
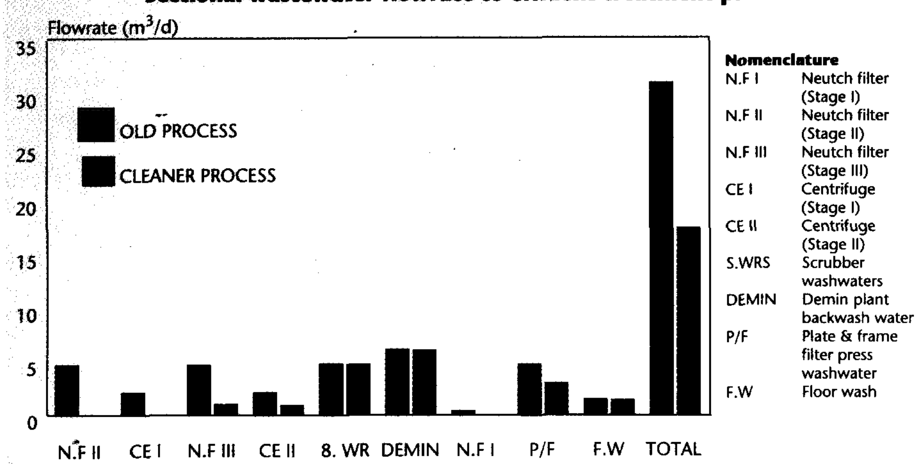


Figure 3
Sectional wastewater flowrate to effluent treatment plant



This clearly indicated that about 3750 kg of amino solution was processed in the Koch acid route in a month. The Koch acid route involved the loss of (around 160 kg/Koch acid batch) intermediate in the Neutch filter filtrate cum washing and centrifuge filtrate cum cloth washing.

Moreover, in the Koch acid route the specific consumption of caustic (0.25 kg of Koch acid/kg of amino solution processed in the Koch acid route) was 7.7 per cent more than that in the amino route. This problem was overcome by installing an additional autoclave of 2000 litre capacity.

The economics of this option are presented in **Table 2**.

The installation of an additional autoclave not only produced annual savings of around Rs. 10.8 lakhs (US$ 36,000), but also eliminated the generation of toxic wastewater streams from second-stage Neutch filter and first-stage centrifuge. The above economic calculation amply demonstrates the payback period for the installation of an additional autoclave to be less than a year.

Recycling

Neutch filtration – stage I (after neutralization)

Washing of the Neutch filter contributed (0.35-0.5 m^3/batch) around 1.5 per cent to the combined wastewater discharge. This was collected in a drum of 500 litre capacity and reused in the neutralization vessel as a make-up for fresh water (around 1500 litres of fresh water was used) in the neutralization vessel.

Filtration in plate and frame filter press

Filter press washing constituted around (4.7 m^3/batch) 15 per cent of the total combined wastewater discharge. On average, about 50 kg of amino solution per batch was lost in the filter press leakages, initial bed scouring and wash-water streams. Around 70 per cent of the total amino loss was recovered by the implementation of the following measures:

◆ A collection tray below the P/F filter press was provided to collect leakages from the P/F interface, which were recycled to reduction vessel.

◆ The wastewater from initial bed loosening (around 0.7 m^3/batch) was filtered over a wooden vat (7 m^3 capacity) in order to filter out the ferric oxide particles, and the clear filtrate was reused as a make-up to the water added in the reduction vessel.

The economics of this recycling is given in **Table 3**.

This recycling operation produced a monthly savings of about Rs 60,000/- (US$ 2000) as against the investment required for the installation of a wooden vat and a recycle pump.

Segregation of toxic concentrated streams

In view of the toxic and non-biodegradable nature of the (low volume and high COD & TDS streams) concentrated streams from the Neutch filter filtrate and centrifuge mother liquor, it was recommended to collect these streams separately at their respective sources and send them to a solar evaporation pond. However Research and Development (R&D) efforts are needed to find out the possibilities of producing cheap quality dyes from these concentrated streams. Due to this simple segregation, the COD load in the residual wastewater treatment stream was reduced by 92 per cent.

The impact of these pollution prevention measures on the production process is depicted in the process block diagram in **Figure 2**.

The impact of the pollution prevention measures described above on the combined wastewater flowrate and COD load is shown in **Figures 3 and 4**.

Areas for further investigation

Process control

The soluble losses of H-acid from Neutch filter filtrate and centrifuge mother liquor are analysed to be around 115 kg/batch. The reasons for this amount of loss are attributed to:

- inherent limitation in the kinetics of various reaction stages which ultimately lead to the formation of isomers;
- improper control of reaction parameters like temperature, pressure, etc.;
- the excessive usage of acids and alkalies starting from sulphonation to isolation step. Due to this, sodium salts (NaCl and Na_2SO_4) get accumulated in the H-acid slurry, further inhibiting the precipitation rate of H-acid in the acidic medium;
- no closer pH control.

By using a digital pH meter (at the time of study, the unit was using pH articles) at each and every reaction stage, excessive addition of acid and alkalies could be brought down. Through closer control of the pH, especially at the isolation step, the H-acid loss in the concentrated streams could also be brought down to a considerable extent. However, this measure requires closer supervision by experts during implementation.

Elimination of gypsum sludge generation[2]

In order to separate the nitro naphthalene sulphonic acid from sulphuric acid, lime and soda ash were used to precipitate the sulphuric acid as calcium and sodium sulphate respectively. This resulted in 11-12 tonnes of gypsum sludge generation per tonne of H-acid manufactured. Gypsum sludge contained 0.5-1 per cent nitro naphthalene compounds.

Through solvent extraction of organic acid from the inorganic acid, followed by distillation system, pure nitro naphthalene sulphonic acid could be produced and the gypsum sludge generation could be eliminated. By means of this technology's adoption, the purity of the H-acid produced will also be high. However, a detailed techno-economic feasibility study has to be conducted to ascertain the application of this technology, to allow the scale of operation prevailing in this unit.

Figure 2
Cleaner production process

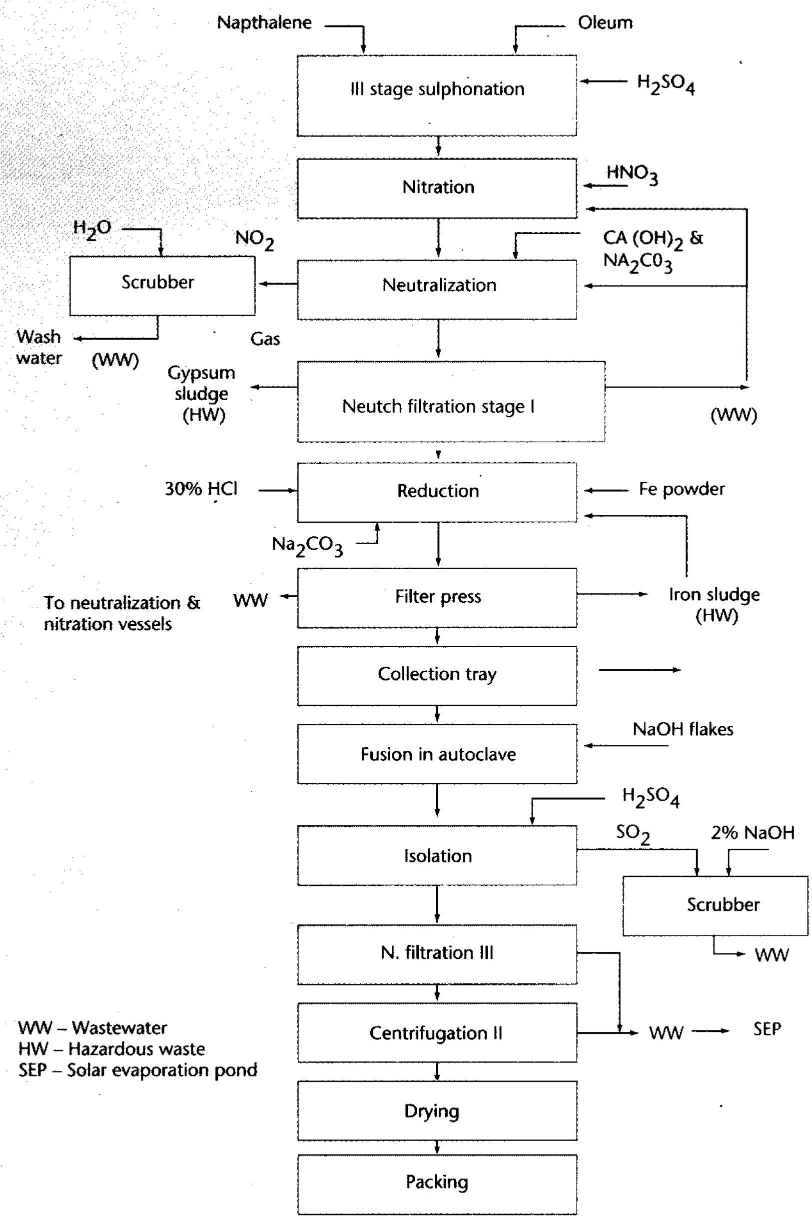


Figure 4
Sectional COD load to effluent treatment plant

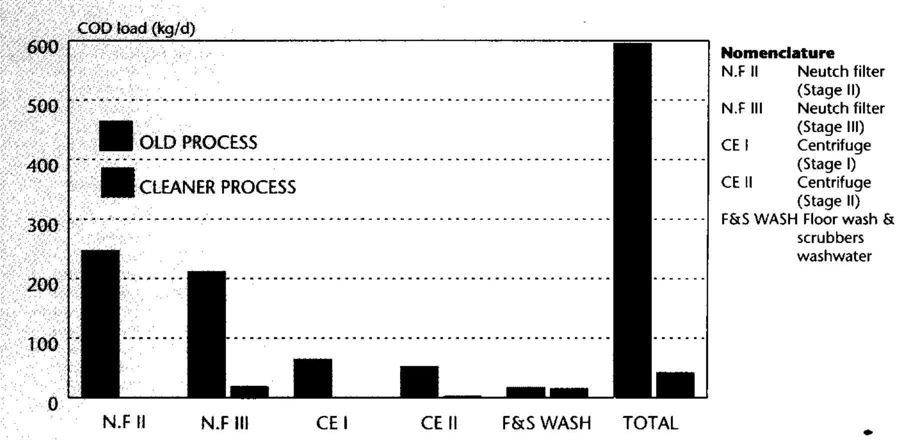


Table 1
Wastewater characteristics

S. No	SOURCE OF WASTEWATER/ INTERMEDIATE PRODUCT	FLOW RATE m^3/d	pH	COD mg/l	NITRO MASS (%)	AMINO MASS (%)	KOCH ACID (%)	H-ACID (%)
1.	Neutch filter I wash water	0.35	6.9	2600	0.24	-	-	-
2.	Plate & frame filter press inlet	-	-	-	-	19.0	-	-
3.	Plate & frame filter press outlet	-	-	-	-	17.0	-	-
4.	Filter press bed washing	4.0	7.4	640	-	-	-	-
5.	Filter press initial charging	0.7	7.3	1212	-	-	-	-
6.	Floor washing	1.4	7.8	4680	-	-	-	-
7.	Second stage Neutch filtrate (5 times/month)	3.6	2.5	50,000	-	-	4.0	-
8.	Second stage Neutch filter washing (5 times/month)	1.12	3.0	20,000	-	-	-	-
9.	First stage centrifuge mother liquor (5 times/month)	1.12	3.0	40,000	-	-	1.4	-
10.	First stage centrifuge cloth washing (5 times/month)	1.0	6.6	6000	-	-	-	-
11.	Third stage N.F. filtrate (mother liquor)	3.55	1.6	42,580	-	-	-	3.7
12.	Third stage N.F. washing	1.12	1.5	19,000	-	-	-	-
13.	Second stage centrifuge M.L.	1.12	1.6	35,680	-	-	-	1.4
14.	Second stage centrifuge cloth washing	1.0	3.2	5230	-	-	-	-
15.	SO_2 scrubber water	0.3	4.0	11,750	-	-	-	-
16.	NO_2 scrubber	4.5	2.5	492	-	-	-	-
17.	Demin backwash	6.1	8.6	224	-	-	-	-
18.	Factory composite	31	2.	1900	-	-	-	-
19.	Factory composite (Neutch filters filtrate and centrifuges mother liquor)	22	5.0	2350	-	-	-	-

Table 2
Economics of installation of an additional autoclave

S. No	DESCRIPTION	STATUS (No of Autoclave) Past (1)	Present (2)
1.	No. of amino route per month	25	30 (at least)
2.	No. of Koch acid route per month	5	0
3.	Amount of amino soln processed (kg/month)	17,500	21,000
4.	Yield of H-acid (kg/month)	9750	10,500
5.	Incremental yield (kg/month)	-	750
	Increase in yield (%) Price of H-acid exclusive of excise duty & freight charges (Rupees/kg)	7.7 120	
	Annual savings (Rupees)	10.8 lakhs	

Note:
Yield of H-acid per kg of amino solution – 0.5 in amino route
Yield of H-acid per kg of amino solution – 0.4 in koch acid route

Catalytic reduction

Iron powder and HCl were used for the reduction of nitro to amino group, resulting in the generation of 3-3.5 tonnes of iron sludge (Fe_2O_3 sludge) per tonne of H-acid. The concentration of amino compound in iron sludge was analysed to be about 4-5 per cent. The amino naphthalene compounds are toxic and carcinogenic in nature. By a catalytic reduction using gaseous hydrogen on the active surface of a metallic catalyst, iron sludge generation could be eliminated.

However, R&D efforts are required in this direction in order to arrive at a cost-effective catalytic reduction system catering to the small scale of operation prevailing in these industries. These efforts will not only increase the present yield and quality of H-acid production, but also eliminate the pollution problem due to high chloride and sulphate contaminate wastewater streams generated from these reaction steps.

Waste exchange opportunities

Reuse of scrubber washwaters

The SO_2 gas generated from isolation step was scrubbed with caustic solution (2 per cent). The concentration of sodium bisulphite in the scrubber water was analysed to be around 8-10 per cent. This stream could be used for the reduction of Cr^{6+} to Cr^{3+} in metal finishing waste treatment. This salt solution could be concentrated and utilized as a reducing agent in the amination step of gamma acid manufacture.

The NO_2 gas generated during nitration reaction was scrubbed with water, resulting in a dilute nitric acid solution. This waste could be transferred to a cold steel rolling mill where it could be used as a make-up for the pickling bath. However, these areas are to be further studied as there is no organized method of waste marketing prevailing in India.

Table 3
Economics of recycling : filtration in plate and frame filter press

Amino loss in the filter press waste	50 kg/batch
Recoverable amino loss due to recycling of bed washing	35 kg/batch
No. of batches carried out/month	30
Amount of amino solution that will be recovered/month	1050 kg
Conversion factor for processing H-acid from amino solution	0.5
Price of 1 Kg of H-acid	Rs 120/- (US$ 4) (Exclusive of excise duty & freight charges)
Estimated monthly savings	Rs 60,000/- (US$ 2000)

Waste processing

The iron (ferric oxide) sludge generated from the reduction step could be used for the production of yellow or red iron oxide pigments. One large-scale dye intermediate manufacturing unit in Gujarat is engaged in the production of iron-oxide pigments from iron sludge generated within the plant. However, the economic viability of this process in small-scale industries is still under exploration.

The concentrated streams from the Neutch filter filtrate and centrifuge were recommended to be used as a raw material in the coupling reaction for cheap quality dye manufacturing.

Conclusion

In India, new governmental policies emphasize cleaner production techniques through waste minimization and exchange.

In this light, these areas would be subjected to in-depth investigation in the forthcoming waste minimization studies. In view of the technical complexity and confidentiality involved in the dyestuff production, it will be more appropriate for the industries to take the onus of working towards pollution prevention, as they only need to be given the "waste minimization perspective".

References

1. *Hazardous Waste Inventorisation in Gujarat,* carried out by National Productivity Council, New Delhi, 1993-1994.
2. *Production Integrated Environment Protection* – Bayer's experience in H-acid manufacturing. ◆

Viewpoint

Otto Soemarwoto, Executive Director, Indonesian Business Council for Sustainable Development, Gedung Wanabakti, Blok IV, Wing B, Lantai 3, Jalan Gatot Subroto, Sonayan, Jakarta 10270, Indonesia

I&E – In *Changing Course*, published in 1992, the Business Council for Sustainable Development (BCSD) argued that the challenge facing industry – and the world – is to achieve "clean, equitable economic growth". Could you describe the overall goals of Indonesian BCSD in this context?

Otto Soemarwoto – Environmental awareness has become a hard reality. Consumers are demanding cleaner production. Hence, producers which do not pay adequate consideration to it will in the not too distant future face difficulties in marketing their products. Indonesian industry will not be an exception. On the other hand, it is also a fact that cleaner production sometimes requires additional costs, even though there are paybacks in the long run. However, if handled well, the additional costs would not be wasted money, but could be earned back in higher profitability and competitiveness. The Indonesian BCSD (IBCSD) aims at creating awareness in the Indonesian business community of the importance of cleaner production in enhancing profitability and competitiveness in domestic and international trade. It also aims at stimulating the adoption of cleaner production by providing information on sources of technology for both large industries and small and medium-sized enterprises (SMEs), and on investment opportunities in sustainable development, as well as by helping industry to establish international contacts with partners who have adopted the eco-efficiency philosophy.

I&E – What specific roles do you see Indonesian BCSD playing in order to increase industry's sensitivity towards sustainable development issues, and to improve dialogue between all the relevant partners in Indonesia?

O.S – Environment in general and cleaner production in particular are being discussed in a very wide circle, including the government, academia, the business community, NGOs and the general public. In general the business community is being blamed as the polluter, as a result of which the business community has adopted a defensive and reactive strategy. IBCSD tries to change this into a proactive strategy in which the business community would take the initiative to create a healthy atmosphere of cooperation with government, academia, NGOs, and the general public. An important step to be taken is, among others, to create dialogue fora to discuss policies, technology, research and technology (R & D), and investment for sustainable development, and to forge cooperation for enhancing the development of cleaner production. Small cross-sectoral discussion groups and larger seminars and workshops have been organized, which also include guest speakers from abroad. An IBCSD newsletter will soon be published. Articles are also being written in newspapers and popular magazines, and in Indonesian scientific journals. Lectures have been given by the Executive Director to business and academic circles. IBCSD is also actively participating in seminars organized by other organizations. Radio and TV lectures are being planned. Special efforts are being made to bridge the credibility gap between industry and NGOs.

I&E – How important is international communication and cooperation for your organization? Do you feel your situation is representative of business organizations working to promote sustainable development in other developing countries?

O.S – With GATT's approval and the creation of the World Trade Organization (WTO), Indonesia cannot afford to be left outside the international community. Indonesia also depends heavily on outside capital and technology. Hence, IBCSD has to develop an active international communication and cooperation programme in order to be able to serve its members, and the business community in general, with up-to-date information on conditions and trends of international environmental politics, the environmental movement, and technology. Otherwise we would be left behind and would lose our competitiveness. I think IBCSD is representative of business organizations in developing countries working to promote sustainable development.

I&E – Environmental management tools are becoming increasingly used in industry – for example, environmental impact assessment, environmental auditing and product life-cycle assessment. ISO will soon issue an "environmental" standard. How does Indonesian industry react to this?

O.S – The general feeling has been that environment is a burden for industry. Recent developments in environmental auditing, life-cycle analysis and eco-labelling are considered as additional pressures from developed countries to preserve their competitiveness. Those pressures are also being felt as unfair, specifically in the case of eco-labelling for tropical forest products. Hence, generally industry is dragging its feet in internalizing environmental costs. However, these pressures are a fact of life and ignoring them would entail very high cost. Consequently, IBCSD is making every effort to convey the message that it is in the interest of industry to become eco-efficient, i.e. to use material and energy more efficiently and thereby reduce both wastes and costs. This seems to be the more effective way, rather than through the teaching of environmental ethics, although this latter should not be ignored.

I&E – Technology transfer is an issue very often discussed on the international scene. What role will BCSD play in that respect? Are there specific developments you would like to see in order to encourage or improve transfer of environmentally sustainable technologies?

O.S – Technology transfer is very important. However, past experience shows that technology transfer has often been used as a means for marketing outdated technology, and hence the gap between the developed and developing countries has not become narrrower, but instead wider. IBCSD, through the World BCSD, is helping industry to seek contacts with partners which are serious about creating a new world of equal partners by providing new cleaner technology and, more importantly, by enhancing the capability of creating new cleaner technology which is appropriate to local conditions. IBCSD is also looking to other international organizations, such as UNEP, in order to be able to access international information at reasonable cost.

I&E – UNEP is promoting a worldwide cleaner production approach aimed at preventing pollution and using raw materials more efficiently. What are the obstacles to implementing this cost-efficient approach widely in Indonesian industry?

O.S – IBCSD warmly welcomes UNEP's worldwide programme on cleaner production. A joint IBCSD, Bapedal (Indonesian Agency for Environmental Impact Management) and UNEP conference will be held in Jakarta in April 1995. A major obstacle is that industry in general is frightened by the deep-rooted image that taking care of the environment is benefiting society, but at the cost of industry. This additional cost, which the SMEs particularly can ill afford, is hampering the creation of awareness that cleaner production is in the interest of industry. Apart from end-of-pipe technology for waste treatment, there is little information on technology for waste minimization, including better housekeeping technology, which in the long run is cost-effective. Another major obstacle is that the government is solely pursuing the command-and-control approach in pollution abatement. Fortunately, there are signs that changes may occur in the near future through also using economic instruments which would stimulate industry towards self-regulation and the adoption of a pro-active strategy in pollution control, and which hopefully would create the right conditions for a *beyond compliance* attitude of industry.

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