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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

WORKING PAPER

19596

95p.

Joint UNDP/UNIDO/APCTT Workshop on
Environmental Considerations and Waste
Recycling in the Chemical, Metallurgical
and Engineering Industries

9 to 13 December 1991, Manila, Philippines

Paper I: Chemical Pollution from Industry-Sources, Emissions and Effects

January 1992

Environmental Resources Limited
106 Gloucester Place, London W1H 3DB
Telephone 071-465 7200
Telex 296359 ERL G
Facsimile 071-935 8355

ERL

[redacted]

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Approved by: Eamonn Barrett.

Position: Technical Director

Date: 14 January 1992

CONTENTS

1 INTRODUCTION

1.1 BACKGROUND

For many years much industrial pollution control has been carried out essentially on an end of pipe basis and a wide range of unit processes (physical, chemical and biological) have been developed to service the needs of industry. Such end of pipe systems range from low intensity to high intensity, from low technology to high technology and from low cost to high cost. Most are destructive processes in that they provide no return to the operating company in terms of increased product yield or lower operating cost except in those circumstances where reduced charges would then apply for discharge to municipal sewer.

It should be noted that in all cases the size (and hence cost) of end of pipe treatment bears a direct relationship firstly to the volume of wastewater to be treated and then to the concentration of pollutants contained in the discharge. It is evident therefore that reduction of emissions by action at source could have a significant impact on the size and hence cost of an end of pipe treatment system.

Source management in isolation however is not likely to provide the total answer to pollution control, and optimised end of pipe control for the irreducible minimum of discharges is required additionally.

The purpose of this Workshop is to identify a method of approach for industry to achieve an optimum strategy for water, wastewater and wastes management and thereby cost effective pollution control through water conservation, reuse and recycle, waste minimisation or avoidance, materials recovery and reuse, application of alternative (cleaner) processes or processing methods or technologies and through optimised end of pipe control.

1.2 SCOPE OF PAPER NO 1

Paper No 1 covers pollution from chemicals arising from the following industries:

- Hides and Skins.
- Pulp and Paper.
- Petrochemicals (Plastics).
- Agrochemicals (Fertilisers and Pesticides).
- Metal Finishing.

- Electronics.

For each industry or industry group the principal issues covered include:

- The Industry and the Environment - a brief statement on the significance of the industry in relation to environmental impact.

- The Industry in Context - a country by country review within the Asia and Pacific region outlining the significance of each industry in each country. For ease of reference the countries are listed alphabetically.

- Production and Processing Methods - a brief review with diagrams of the principal production and processing steps which require input of chemicals and which generate emissions to the aqueous environment, to land or to air.

- Use/Generation of Chemicals - a brief description with diagrams summarising the principal chemical inputs and pollution outputs.

- Emissions and Effects - quantification of emissions and a summary of principal impacts.

Paper No 1 is designed to be read in conjunction with Paper No 2, the latter having the objective of identifying a procedure by which effective pollution control can be achieved through a combination of:

- integrated source control; and
- optimised end of pipe control.

2 *POLLUTION FROM THE HIDES AND SKINS INDUSTRY - SOURCES, EMISSIONS AND EFFECTS*

2.1 *THE INDUSTRY AND THE ENVIRONMENT*

The hides and skins processing industry is one of the world's oldest. It involves conversion of raw or semi-processed hides to a stable end product through various cleaning, preparation and finishing processes designed to stabilise the proteins in the hide to make it insoluble in water and at the same time giving it the tough and flexible characteristics of leather. A similar conversion is carried out on skins. The principal stabilisation process is known as tanning.

The industry is carried out in most parts of the world. However in many areas the processing of hides and skins remains a labour intensive industry employing traditional methods.

Large quantities of water are used by the industry; generally in the range 30 to 50m^3 per tonne of wet salted hide processed. In addition, large quantities and a wide variety of chemicals are used, the likely range between 25 and 40 depending on the type and size of establishment and the nature of the processes carried out. It is estimated that chemicals represent up to 25 percent of the total cost of leather manufacture.

The tanning industry has long been characterised as 'noxious' due to the high quantities of waste produced, both solid and aqueous; also because of related noxious odours.

For example, for each tonne of wet salted hide processed, less than 200 kg of leather is produced. Waste products include:

- constituents of the raw hide which are necessarily removed or modified during the cleaning and preparation processes (dissolved and insoluble) including various proteins, fats, trimmings, etc and the specific chemicals used in the preserving (curing) process;

- surplus and residual chemicals from the pre-tanning and tanning processes.

Typical tannery wastewater contains large amounts of solids, both dissolved and suspended, and inorganic and organic; also significant amounts of sulphide and chromium.

A tannery wastewater has a population equivalent of about 1000 per tonne of wet salted hides processed when calculated on the basis of a typical wastewater production factor of 40m^3/t wet salted hides, a typical organic content of 1500mg/l as Biochemical Oxygen Demand (BOD) and comparing this to a typical per capita contribution of 0.055 kg BOD per day.

Tanneries can be categorised into:

- Small - less than 100 hides per day.
- Medium - 100 to 1,000 hides per day.
- Large - more than 1,000 hides per day.

The industry can have a major impact on the environment. It is known to be very polluting especially through effluents high in organic/inorganic dissolved and suspended solids content and containing potentially toxic metal salt residues. Such effluents can cause substantial oxygen depletion in the receiving waters, also a deleterious and toxic effect on aquatic organisms.

Disagreeable odours emanating from the decomposition of protein solid waste, the release of hydrogen sulphide, ammonia and volatile organic compounds are also environmental impacts of concern.

Accordingly, the disposal of waste from hides and skins processing establishments must be carefully planned if environmental damage is to be mitigated.

In an effort to control pollution in recent years, the introduction of improved technologies into modern plants has brought increased efficiency together with methods to enable the effective control of waste quantities.

2.2 *THE INDUSTRY IN CONTEXT*

2.2.1 *Bangladesh*

The gross value of leather and leather products in Bangladesh has increased from TK 2565 million in 1983/84 to TK 4,713 million in 1987/88. From figures shown in *Table 2.2a*, Bangladesh appears to be a nett exporter of leather.

Table 2.2a *Value of Leather Imports and Exports, 1987*

Product	Value (US$ million)	
	Imports	Exports
Calf leather	0.0	8.8
Other leather, including artificial	0.0	118.2
Leather manufactures	0.1	0.0
Apparel and accessories of leather	0.0	0.0

Source: UNIDO, 1991

2.2.2 *China*

The leather industry in China primarily bases its products on oxhide and hogskin. Production levels have remained reasonably constant over recent years, with latest figures from the State Statistical Bureau of the People's

Republic of China (1990) indicating a 1989 production of 52 million pieces (oxhide equivalent).

Leathers, furs and their related products occupy a reasonably significant proportion of China's manufacturing output, with the number of enterprises in 1989 totalling 7761. Gross output value was 17.5 billion yuan. Most export destinations were to developing countries and the US, and the overall export/import situation is summarised in *Table 2.2b* below.

Table 2.2b ***Value of Leather Imports and Exports, 1989***

Product	**Value (US$ million)**	
	Imports	**Exports**
Calf leather	0.2	0.0
Other leather, including artificial	163.8	57.4
Leather manufactures	94.5	22.7
Apparel and accessories of leather	1.8	330.5

Source: UNIDO, 1991

A large proportion of the industry is concentrated in the regions of Jiangsu, Zhejiang, Henan, Guangdong and Sichuan, as shown by *Table 2.2c*. There has been some priority given to utilising foreign investment and advanced technology, and this will affect the hides and skin industry in the following areas:

- product design improvements;
- setting up of external sales and information networks;
- more advanced machinery and testing instruments for use in the technical transformation of existing enterprises.

Table 2.2c *Gross Output Value of Leather, Furs and Their Related Products*

Region	Number of Enterprises	Gross Output Value (1,000,000,000 yuan)	
		At 1980 Constant Prices	At Current Prices
Beijing	83	0.357	0.520
Tianjin	155	0.411	0.579
Hebei	386	0.514	0.696
Shanxi	119	0.130	0.170
Inner Mongolia	245	0.252	0.365
Liaoning	336	0.458	0.676
Jilin	194	0.196	0.304
Heilongjiang	282	0.348	0.486
Shanghai	174	0.820	1.321
Jiangsu	739	1.577	2.095
Zhejiang	1041	1.097	1.588
Anhui	286	0.281	0.402
Fujian	178	0.337	0.426
Jiangxi	221	0.177	0.236
Shandong	394	1.274	1.598
Henan	367	0.568	0.858
Hubei	347	0.387	0.462
Hunan	432	0.420	0.5[illegible]1
Guangdong	508	1.743	2.122
Guangxi	76	0.130	0.208
Hainan	11	0.006	0.006
Sichuan	517	0.455	0.689
Guizhou	96	0.062	0.084
Yunnan	88	0.093	0.132
Tibet	6	0.005	0.006
Shaanxi	129	0.135	0.195
Gansu	107	0.151	0.219
Qinghai	33	0.048	0.088
Ningxia	40	0.033	0.046
Xinjiang	171	0.204	0.376
National Total	**7761**	**12.670**	**17.532**

Source: State Statistical Bureau of the Peoples Republic of China, 1990

2.2.3 *India*

The leather industry in India has its roots in the small and cottage sectors. Processing of hides and skins is done using old techniques in over 10,000 centres in different states. The greatest concentration is in Uttar Pradesh, Tamil Nadu, West Bengal, Karnataka and Maharashtra.

In the 1950s and 1960s there was no attempt to produce finished leather and as a result, shipments were mainly in the form of processed hides and skins and semi-finished leather. Due to the added value of finished product exports, greater emphasis has recently been placed on finished leathers, leather footwear, goods and garments.

Raw materials for the leather industry are available in large quantities due to the huge cattle population. However, methods of recovery of hides and skins from carcasses and slaughtered animals are primitive and processing techniques are outdated. In order to improve quality, it has been necessary to induct new technology to train workers to obtain the best out of the available raw materials. Polyurethane treatment has been suggested to upgrade inferior hides and skins.

Although full details of the cottage industries are not available, they are estimated to process around 11.8 million pieces of hides and 0.4 million pieces of skins out an industry total of 34.0 million pieces and 71.4 million pieces respectively. There are 65 firms in the organised sector accounting for 8.1 million hides and 55.9 million skins, 77 licensed small-scale industries with a shore of 6.1 million hides and 11.2 million skins, and 800 unlicensed small-scale enterprises processing 8.0 million hides and 3.9 million skins.

A summary of imports and exports is provided in *Table 2.2d*

Table 2.2d ***Value of Leather Imports and Exports, 1987***

Product	**Value (US$ million)**	
	Imports	**Exports**
Calf leather	1.1	137.1
Other leather, including artificial	10.7	320.7
Leather manufactures	7.1	266.4
Apparel and accessories of leather	0.0	95.8

Source: UNIDO, 1991

2.2.4 *Indonesia*

Production of leather in Indonesia has grown significantly in the last decade, with the value increasing from Rp 1404 million in 1975 to Rp 14871 million in 1985. The leather processing industry is characterised by very high total labour requirements and therefore contributes substantially to the local community in a number of Provinces. These Provinces include West Java, South Kalimantan, South Sulawesi and Bali.

The export of leather is reasonably small in comparison to areas such as textiles, petroleum and non-ferrous metals, and primarily centred on US destinations. Figures for 1989 are summarised in *Table 2.2e*.

Table 2.2e *Value of Leather Imports and Exports, 1989*

Product	Value (US$ million)	
	Imports	Exports
Calf leather	1.4	32.0
Other leather, including artificial	31.9	35.6
Leather manufacures	25.1	4.4
Apparel and accessories of leather	0.6	9.8

Source: UNIDO, 1991

2.2.5 *Iran*

As shown in *Table 2.2f*, trade in this manufacturing subsector in Iran is negligible.

Table 2.2f *Value of Leather Imports and Exports, 1977*

Product	Value (US$ million)	
	Imports	Exports
Calf leather	6.5	0.0
Other leather, including artificial	6.6	0.0
Leather manufactures	1.1	0.0
Apparel and accessories of leather	0.8	0.0

Source: UNIDO, 1991

2.2.6 *The Republic of Korea*

The textile, apparel and leather industry has played a critical role in The Republic of Korea's initial industrialisation since the 1960s. Although government policy subsequently accorded most priority to developing the heavy industries, electronics and high-tech industries, the textile, apparel and leather sector has continued to make a substantial contribution to overall manufacturing production.

Gross output in leather products has increased from Won 107 billion in 1975 to Won 2013 billion in 1989. A significant proprotion of this production was exported, as shown in *Table 2.2g*.

Table 2.2g *Value of Leather Imports and Exports, 1989*

Product	Value (US $ million)	
	Imports	Exports
Calf leather	5.2	1.3
Other leather, including artificial	606.9	192.8
Leather manufactures	34.7	126.9
Apparel and accessories of leather	7.1	2017.2

Sources: UNIDO, 1991

2.2.7 *Malaysia*

The hides and skins industry in Malaysia is of small significance in comparison to overall trade volumes, and in general is fairly balanced between imports and exports. This relationship is shown in *Table 2.2h*.

Table 2.2h *Value of Leather Imports and Exports, 1988*

Product	Value (US$ million)	
	Imports	**Exports**
Calf leather	2.2	2.2
Other leather, including artificial	3.8	1.1
Leather manufactures	2.3	4.9
Apparel and accessories of leather	1.1	0.1

Source: UNIDO, 1991

2.2.8 *Pakistan*

Pakistan's earnings from leather products have increased markedly in dollar terms over the past few years, with it now accounting for 5% of the world's leather exports. The strong growth performance seen in recent years is expected to continue well into the 1990s.

Table 2.2i *Value of Leather Imports and Exports, 1988*

Product	Value (US$ million)	
	Imports	**Exports**
Calf leather	0.2	43.8
Other leather, including artificial	4.9	223.2
Leather manufactures	0.3	5.4
Apparel and accessories of leather	0.1	136.8

Source: UNIDO, 1991

2.2.9 *The Philippines*

Similarly to Malaysia, the hides and skins industry in The Philippines occupies a reasonably small area of the total manufacturing sector. The relationship between imports and exports is summarised in *Table 2.2j*.

Table 2.2j *Value of Leather Imports and Exports, 1988*

Product	Value (US$ million)	
	Imports	**Exports**
Calf leather	0.4	0.0
Other leather, including artificial	11.5	0.3
Leather manufactures	3.3	2.0
Apparel and accessories of leather	0.4	11.7

Source: UNIDO, 1991

2.2.10 *Sri Lanka*

Origins of imports and exports in the leather and skins industry in Sri Lanka are shown in *Table 2.2k*.

Table 2.2k ***Value of Leather Imports and Exports, 1987***

Product	Value (US$ million)	
	Imports	Exports
Calf leather	0.2	0.0
Other leather, including artificial	3.0	1.0
Leather manufactures	0.3	0.4
Apparel and accessories of leather	0.1	4.7

Source: UNIDO, 1991

2.2.11 *Thailand*

Origins of imports and exports in the leather and skins industry in Thailand are shown in *Table 2.2i*. From the results shown, it appears Thailand has a buoyant hides and skins industry.

Table 2.2i ***Value of Leather Imports and Exports, 1987***

Product	Value (US$ million)	
	Imports	Exports
Calf leather	0.0	0.0
Other leather, including artificial	22.5	55.8
Leather manufactures	3.3	78.5
Apparel and accessories of leather	0.4	21.2

Source: UNIDO, 1991

2.3 *PRODUCTION AND PROCESSING METHODS*

2.3.1 *Introduction*

Hides and skins processing establishments can be subdivided according to:

- the basic type of raw material (hides and skins);
- the type of tanning agent used ie chrome tanning or vegetable tanning; or
- the degree to which leather or end product processing is carried out and thereby the degree to which waste and wastewater is produced, eg
  - full finished in which raw material is processed to full finished leather;

- 'wet blue' in which raw material is processed to the (chrome) tanning stage.

The range of unit processes generally carried out in the hides and skins industry is depicted diagrammatically in *Figure 2.1*.

2.3.2 *Curing of Hides and Skins*

In most developed countries hides and skins are removed and lightly cured with salt at abattoirs or local hide collection centres; throughput is relatively regular and technical supervision is available. The hides and skins then enter commercial channels and are transported, generally relatively short distances, to tanneries for processing.

However, in many developing countries most animal slaughter takes place at rural locations. The production of hides and skins is usually at a low and erratic volume governed by seasonal conditions and accordingly in these circumstances only minimal supervision may be available at the curing site. With the high ambient temperatures often encountered curing is not simple. Salt, if available, is applied to 30 to 50 percent of raw (green) weight and the skins then dried (dry salting). Alternatively salt curing is carried out in the wet stage ie 'wet salting' whereby the hide is immersed and saturated with brine solution.

In countries deficient in cheap salt supplies, curing is by controlled shade drying (varying conditions and degrees of drying). However unless such drying is well controlled, degradation of the hides and skins may occur. The major drawback of 'drying' is that the tanner must subsequently attempt to reverse the process (rehydrate) during soaking (employing large volumes of water). Curing often incorporates treatment with insecticides to discourage beetle and other insect attack during storage and transport.

2.3.3 *Soaking*

Soaking is performed to rehydrate the skin and to reverse the cure process; also to remove salt. Soaking may take up to 48 hours, depending on the degree and type of cure and ambient temperature. Dirt, blood and dung will also be removed.

2.3.4 *Scouring (of skins)*

Depending on the source skins can contain significant quantities of grease. Its removal is achieved by washing in hot water/detergent to emulsify the grease.

2.3.5 *Liming*

The liming process utilises large quantities of lime blended with sodium sulphide to loosen wool and hair or dissolve these into a pulp; additionally the process opens the fibre structure.

For skins with hair of wool of potentially high value, depilation is effected by 'painting' the flesh side of the hide or skin with a mix of lime or kaolin plus sodium sulphide. After processing for some hours the hair roots are attacked and the wool removed without being seriously contaminated by chemicals. Such 'hair save' processes however need a subsequent liming stage (alkaline treatment, possibly sulphide free) to accomplish the necessary adjustments to fibre structure.

Hides and skins may be split in the limed condition. However due to technical difficulties the 'splitting' process is often carried out in the tanned condition.

2.3.6 *Fleshing*

Fleshing involves the physical removal of adipose tissues from the flesh side of the hide. (The resultant fleshings are difficult to handle due to their mucous-like condition and the unavoidable presence of large volumes of water from the machine).

2.3.7 *Delime*

Deliming involves the removal of lime from the hide which is not always completed through the full thickness of the hide. Copious washing is followed by neutralising chemicals.

2.3.8 *Bating*

Bating is an enzymatic process which has pronounced effect on the grain of the hide or skin.

2.3.9 *Pickling*

Pickling involves an adjustment of the pH of the pelt, sterilising the skin, ending the bating action and allowing penetration prior to subsequent fixation of the tanning material.

2.3.10 *Tanning*

The tanning process converts the collagen, the major constituent of the hide, into a non-putrescible condition. In addition, tanning imparts the necessary 'feel' and chemical and physical characteristics to the leather. Options include:

- *chrome tanning* - the majority of leathers are today chrome tanned.
- *vegetable tanning* - is still employed for sole and saddlery and some speciality leathers.
- *Syntans* - are employed as auxiliaries in association with chrome and vegetable tanning or in isolation for certain speciality leathers.

A wide variety of alternative tanning materials are also available for use as primary materials or as auxiliaries.

2.3.11 *Post Tanning Activity*

Following tanning certain physical operations are carried out including pressurised rolling to remove excess moisture, splitting (by machine) if not already carried out and shaving (levelling).

2.3.12 *Neutralise, Retan, Dye, Fat Liquor*

During these processes, often sequential, employing a common bath, the final colour, feel and characteristics of the leather are obtained. The processes employ:

- *Neutralising* - Mild alkali or Syntan.
- *Retan* - A range of tanning materials.
- *Dye* - Acid, direct, basic or speciality dyes.
- *Fat Liquor* - Sulphated or sulphonated fish, vegetable or animal oils, as well as mineral and 'synthetic' oils.

2.4 USE/GENERATION OF CHEMICALS

Chemicals typically in use in the hides and skins industry are listed in *Figure* 2.2. Most appear in the wastewater discharged (in original or modified form) together with those constituents of the hide and skin which are dissolved or removed during the cleaning, preparation, tanning and finishing processes.

In addition to the specific chemicals listed as raw materials, other 'chemical' and component discharges include:

- fats and grease
- proteinaceous matter
- sodium chloride
- insecticides (possibly derivatives of chlorinated aromatic compounds but also arsenic and mercury based insecticides)
- dirt grit etc.

Water usage is typically 30 to 40m^3 per tonne of wet hides processed, or 25 to 35m^3 per tonne of limed pelt. However, accurate calculation of specific water usage is difficult due to the number of process variations, particularly with respect to the wide range of differing cure conditions.

2.5 EMISSIONS AND EFFECTS

2.5.1 *Emissions to Aqueous Environment*

Volumes of water utilised in the hides and skins industry has been lowered in recent years from in excess of 100 to about 40m^3/t wet hides processed. This has been brought about through:

- increased charges for water supplies;
- attempts to reduce volume and subsequent charges for effluent treatment;
- introduction of tanning technology to obtain more efficient utilisation of process chemicals and more rapid production techniques.

Aqueous emissions can be characterised in terms of:

- constituents of the hide which have been attacked or reconstituted during processing;
- specific pollution loads calculated per unit weight of hides processed;
- typical pollution concentrations in mg/l.

Constituents of the hide which appear in aqueous emissions are summarised in *Table 2.5a* below

Table 2.5a *Aqueous Emissions - Minimal Inevitable Pollution*

	Pollution kg/tonne wet salted hide
Inorganic solids	
• Hide salt	150
• Others	10
Total inorganic	160
Organic solids	
• Hair protein	40
• Hide protein	25
• Hide fat and carbohydrates	15
• Dirt and manure	5
• Others	5
Total inorganic	90
TOTAL SOLIDS	250

Source: UNIDO, 1984

In practice, normal tannery effluents contain at least double the theoretical minimum due to the discharge of appreciable surplus of process chemicals.

Typical variations in specific pollutants produced expressed as kg/tonne of raw slated hide are summarised in *Table 2.5b* below.

Table 2.5b ***Aqueous Emissions - Typical Pollutant Loads***

	kg/tonne wet salted hide				
	UNIDO chrome	**USA chrome**	**France chrome**	**Sweden Mixed**	**Poland Mixed**
BOD (kg/t)	60	95	75-90	71	70
COD (kg/t)	175	260	200-220	190	233
Suspended solids (kg/t)	150	140	140	106	70
Sulphide (kg/t)	7	8.5	9	-	6
Chromium (kg/t)	4.5	4.3	6	2.7	1.1
Water (m^3/t)	45	53	65	40	70

Source: UNIDO, 1984

Typical variations in specific pollutants expressed as concentrations are summarised in *Table 2.5c* below.

Table 2.5c ***Aqueous Emissions - Typical Pollutant Concentrations***

	UNIDO chrome	**USA chrome**	**France chrome**	**Sweden Mixed**	**Poland Mixed**
BOD (mg/l)	1333	1800	1270	1775	1000
COD (mg/l)	3890	4900	3230	4750	3615
Suspended solids (mg/l)	3333	2640	2150	2650	1000
Sulphide (mg/l)	155	160	140	-	86
Chromium (mg/l)	100	80	93	68	16

Source: Calculated from *Table 2.5b*

Aqueous emissions have major environmental impacts in relation to the potential toxicity of two specific constituents, chromium and sulphide, also the overall biological load which could have significant localised effect on the dissolved oxygen content of a receiving water.

Chromium in the hexavalent form is reported to have some adverse effect on aquatic life. Although fish are relatively tolerant towards chrome, fish food organisms and other lower forms of aquatic life tend to display increased sensitivity. However, tannery discharges contain chromium in the less toxic trivalent form, and at typical discharge pH of 8-10 (mixed liquors) such chromium would be in a precipitated form (although resolubilisation cannot be ruled out).

In addition to the noxious odour and unpleasant taste which can be imported to receiving waters, the major effects of sulphide are:

- decreases in dissolved oxygen content of waters, with possible effects on all forms of aquatic life;

- possibility of causing dark coloured precipitates in the presence of some metals (eg iron);

- increased toxicity to fish at lower pH's.

Of major importance is the toxicity to humans of hydrogen sulphide gas. In addition it should be noted that in the confined space of sewer systems H_2S gas may dissolve in the water film on walls and be bacterially oxidised to form sulphuric acid which may attack the fabric of the sewer.

The effect of the discharge of the general mixed wastes is a function of the level of dilution afforded by the receiving watercourse. The major effect of a discharge of this 'biological load' is noticed by lowering of the dissolved oxygen (DO) content of the receiving water which could adversely and readily affect aerobic aquatic life.

Although wastewaters from the industry vary widely in pH value, organic content and mineral composition, they can be treated by conventional end of pipe treatment methods such as oxidation ponds or the activated sludge process, to considerably reduce the polluting load on the environment.

Preliminary treatment will involve balancing, pH control and sedimentation or flotation (with or without chemical addition). Balancing can be combined with aeration to oxidise sulphide (using manganese chloride as catalyst). Chromium will be largely transferred to sludges and disposed of as solid wastes.

2.5.2 *Emissions to Land*

The volumes of solid wastes produced are highly dependent on the raw material being worked and of the nature of the end-product. There is little published data comparing solid waste production from differing raw materials.

A UK Department of Environment Paper provides the following materials balance expressed as kg/tonne of wet salted hide for production of chrome tanned leather.

- Trimmings - 120.
- Fleshings - 70 to 230.
- Chrome shavings - 99.
- Chrome split waste - 115
- Buffer dust - 2.
- Finished trimmings - 32.
- Effluent sludge - 250.

This indicates a total of between 688 to 848 kg solid waste (as produced) per 1000 kg of wet salted hide. This equates to about 500 kg of solid waste on a dry weight basis per 1000 kg of wet salted hide.

The solid wastes from tannery production vary greatly in character according to the technology employed and the levels of 'housekeeping' instituted within the tannery.

The most significant solid wastes are as follows:

- Untanned collagenous wastes and fats as raw and soaked trimmings and fleshings.

- Sulphide bearing wastes such as trimmings and fleshings from the hide in limed condition and beamhouse residues and sludges.

- Chrome bearing wastes such as shavings, buffing dust and sludges from equalised effluents.

The untanned wastes, with their high protein and fat content can, if let lying in damp conditions, give rise to odours due to bacterial attack and decomposition as well as encouraging beetle and insect infestation. Often disposal is to landfill but this is not always satisfactory due to slow degradation. In addition, the water penetration characteristics of the landfill site are adversely affected.

However, provided they are not heavily contaminated with process chemicals, such wastes are considered to be suitable material for agricultural fertiliser and, if rapidly removed from the tannery and dug or ploughed into agricultural lands, the wastes rapidly disintegrate and do not cause odour or other significant environmental impacts.

Until the last decade there were significant economic demand for fleshings, trimmings and untanned splits for use as a basis for fat rendering and in the manufacture of glue and gelatine. However, with the advent of synthetic glues and detergents, demand for tannery fallow in most countries has reduced.

Untanned wastes bearing sulphide, if accumulated, may give rise to malodorous hydrogen sulphide fumes. However the concentration in this form is not considered to be hazardous and degradation will be minimal if the material is regularly removed from the site to landfill or agricultural disposal. Beamhouse residues and sludges also can be buried but as the means now exists to remove the majority of sulphide from such sludges, sulphide bearing material need not necessitate a specific disposal plan.

Chromium bearing wastes are generally disposed of to landfill as opposed to agricultural disposal. The toxicity of tannery solid wastes due to the presence of chromium often is raised as a detraction to agricultural land disposal. Many earlier comments regarding chromium toxicity refer to chrome in the hexavalent form whereas the vast majority of tanneries today employ the less toxic trivalent form of chromium. Sludges from effluent treatment could contain up to 3.5 percent chromium as Cr whereas other chromium bearing wastes could contain between 2 to 5 percent chromium as Cr.

2.5.3 *Emissions to Air*

Odour nuisance is ubiquitous at sites processing hides and skins and is difficult to control except by adopting improved technology. Emission of hydrogen sulphide, as noted above, is not only a nuisance but is potentially lethal.

Of major importance is the toxicity to humans of hydrogen sulphide gas. In this respect it must be noted that if the pH of a sulphide bearing liquor is allowed to fall below pH 8.5 appreciable volumes of toxic H_2S gas will be discharged, with possibility of human fatality. Such incidents have caused fatalities in 'on site' effluent treatment vessels holding lime liquor. Wastewaters containing sulphide should therefore be kept separate from acidic wastes, and oxidised by air as described above.

Figure 2.1 *The Hides and Skins Industry*

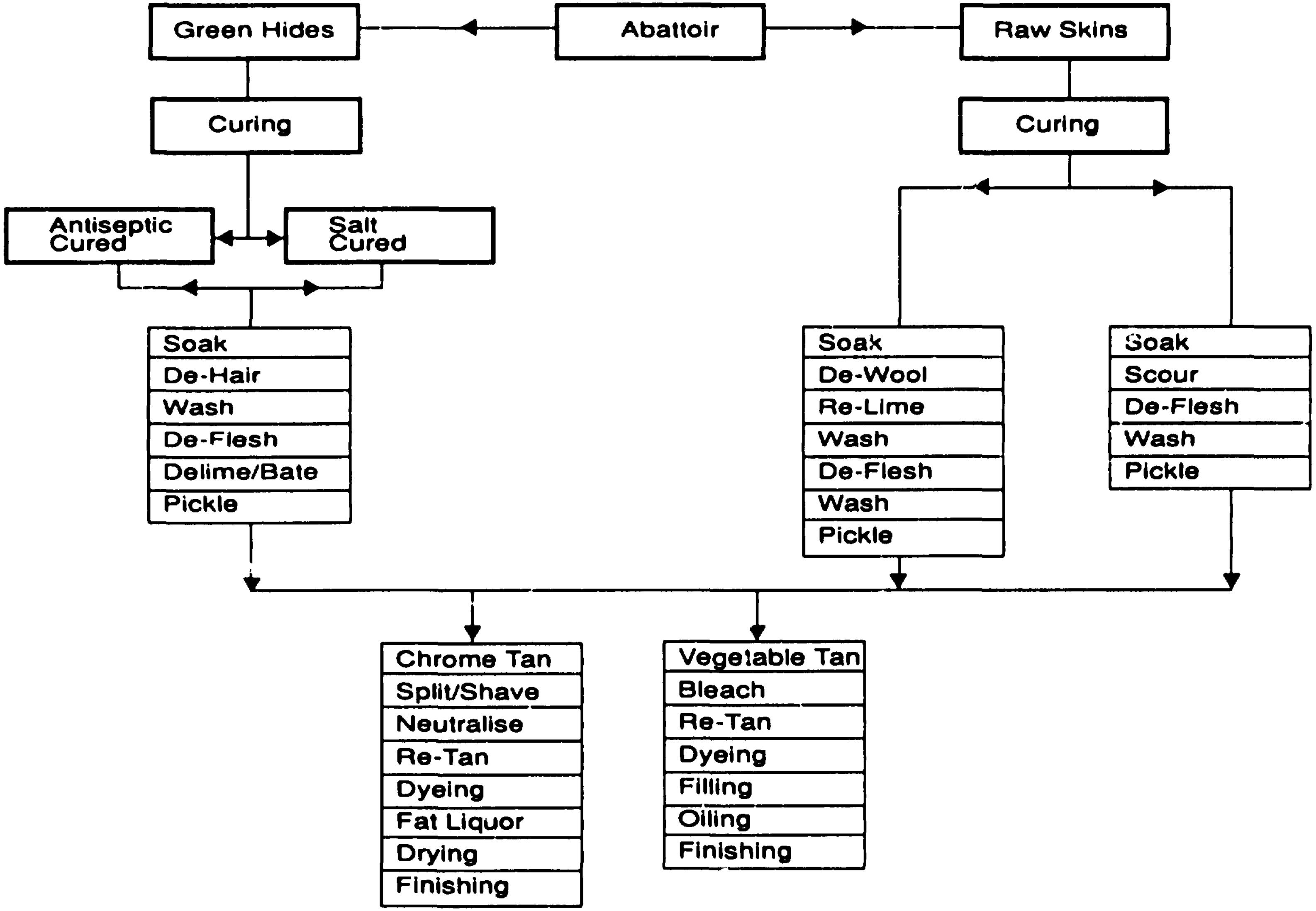
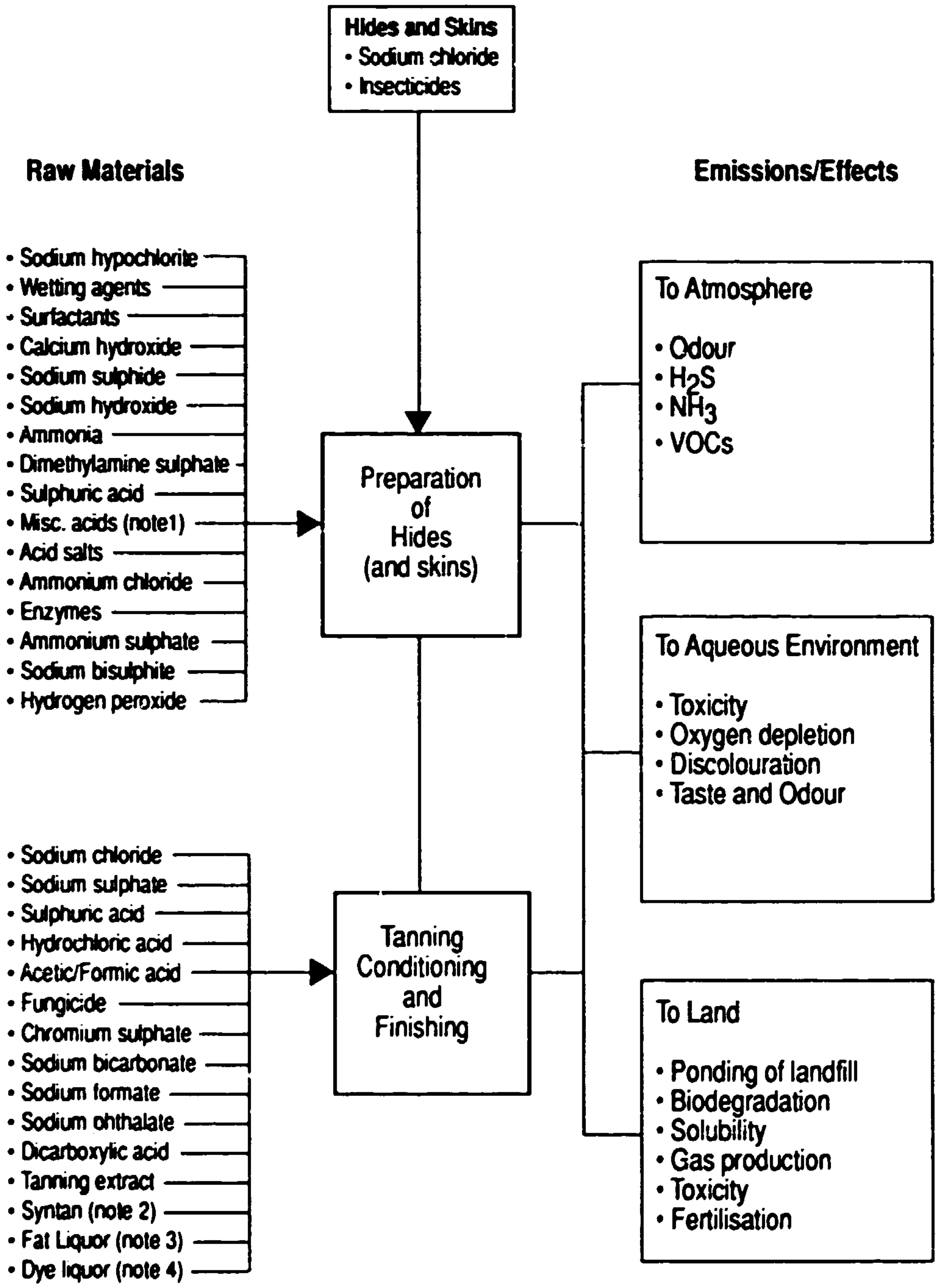


Figure 2.2 *Raw Materials and Emissions The Hides and Skins Industry*



Note 1: Hydrochloric, lactic, formic, boric acids

Note 2: Sulphonated condensed products of phenol

Note 3: Sulphated or sulphonated fish, vegetable or animal oils

Note 4: Acid, direct, basic or speciality dyes

3 POLLUTION FROM THE PULP AND PAPER INDUSTRY - SOURCES, EMISSIONS AND EFFECTS

3.1 THE INDUSTRY AND THE ENVIRONMENT

The basic raw materials used in pulp manufacture are renewable lignocellulosic fibrous materials. In developed countries woods are primarily used for pulping. However in many developing countries wood is in short supply and more than 45 percent of the pulp is manufactured from other fibrous materials, mainly agricultural residues such as straw, bagasse and bamboo.

Both chemical and mechanical processes are used in pulp production. Among the chemical processes, the kraft process for wood and the soda process for non-wood pulping predominate. Both operate in alkaline conditions.

The basic steps for pulp production are:

- fibrous raw material preparation;
- pulping;
- screening;
- washing;
- bleaching; and
- recovery of chemicals (chemical pulping only).

The paper industry uses virgin fibres produced by pulping of lignocellulosic fibrous raw materials, a considerable amount of recycled fibres (waste paper), and non-fibrous materials (chemicals, minerals eg china clay).

The industry can have a major impact on air, water and land; however the extent of this impact can, in part, be controlled by appropriate technology and many pulp and paper mills have reduced emissions to a small fraction of levels several years ago. It should be recognised that there are still significant technical and economical difficulties in pollution abatement, particularly in collecting and burning black liquor and recovering chemicals in small pulp mills.

3.2 THE INDUSTRY IN CONTEXT

3.2.1 *Bangladesh*

Information from the Economist Intelligence Unit (Bangladesh Country Profile, 1991/92) indicate that production of paper and paper products is increasing, with the gross value of production from this sector rising from TK 1959 million in 1983/84 to TK 2861 million in 1987/88. Demand exceeds local production, and exports are negligible. Figures on the composition and value of trade in pulp and paper products are provided in *Table 3.2a*.

Table 3.2a ***Composition and Value of Pulp and Paper Trade, 1987***

Product	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Pulp paper, including waste	0.6	15.1	0.0	0.0
Paper and paperboard	0.7	17.2	0.0	0.0
Articles of pulp, paper or paperboard	0.2	5.0	0.0	0.0

Source: UNIDO, 1991

3.2.2 *India*

Private investors have made a massive investment in the paper industry, building three large paper mills and subsequently increasing capacity from 1.66 million tonnes in 1981/82 to 2.45 million tonnes in 1984/85. However, actual 1984/85 output of paper and board was only 1.36 million tonnes (The Economist Intelligence Unit, 1986) and capacity utilisation showed substantial decreases. The main problems faced by the industry are reliable power and coal supplies, and a growing shortage of raw materials. It is projected that high imports will be required to alleviate a future paper famine.

With regard to newsprint, demand has risen from 1984/85 levels of 185,000 tonnes to 295,000 tonnes in 1989/90. A simultaneous increase in production has meant that imports have remained fairly constant. The composition and value of pulp and paper trade is shown in *Table 3.2c*.

Table 3.2c *Composition and Value of Pulp and Paper Trade, 1987*

Product	Imports		Exports	
	% of Total Trade	Value (US$ million)	% of Total Trade	Value (US$ million)
Pulp paper, including waste	1.1	184.0	0.0	0.0
Paper and paperboard	1.2	201.4	0.0[1]	3.1
Articles of pulp, paper or paperboard	0.0	5.9	0.0[1]	2.4

[1] Rounding errors

Source: UNIDO, 1991

3.2.3 *Iran*

It appears that Iran is not self-sufficient in this sector, and relies on small volumes of imports. The trade situation is summarised in *Table 3.2e*.

Table 3.2e *Composition and Value of Pulp and Paper Trade, 1987*

Product	Imports		Exports	
	% of Total Trade	Value (US$ million)	% of Total Trade	Value (US$ million)
Pulp paper, including waste	0.1	20.6	0.0	0.0
Paper and paperboard	1.2	173.9	0.0	0.0
Articles of pulp, paper or paperboard	0.3	41.7	0.0	0.1[1]

[1] Rounding errors

Source: UNIDO, 1991

3.2.4 *Pakistan*

The paper and printing subsector of manufacture in Pakistan is subject to substantial regional variations in output, with most gross output being concentrated in Sind. Punjab and the North-West Frontier Province together have a gross output approximating Sind, and Baluchistan is substantially less. This is to be expected, due to the very low overall contribution of the Baluchistan region to Pakistan's fixed manufacturing assets.

Pakistan has a net trade deficit in the pulp and paper sector, as illustrated in *Table 3.2h*. However, there is considerable potential in the Punjab region for expansion of paper milling operations, and this may reduce the country's dependence on imports in future years.

Table 3.2h *Composition and Value of Pulp and Paper Trade, 1988*

Product	Imports		Exports	
	% of Total Trade	Value (US$ million)	% of Total Trade	Value (US$ million)
Pulp paper, including waste	0.3	18.7	0.0	0.0
Paper and paperboard	1.9	124.3	0.0	0.0
Articles of pulp, paper or paperboard	0.2	10.0	0.0	0.4[1]

[1] Rounding errors

Source: UNIDO, 1991

3.2.5 *The Philippines*

The pulp and paper industry in the Philippines employs about 13000 people working in 23 paper and board mills and three pulp mills. Major products in the paper and board sub-group are newsprint, woodfree paper, kraftliner, other wrapping papers and board, whereas in the pulp sub-group bleached and unbleached sulphate dominate. The most recent addition to capacity is a new mill built in the province of Pampanga. This mill primarily uses wastepaper for the production of 35,000 tonnes of printing/writing papers of various grades.

Main problems of the industry include outdated machinery and equipment, high fuel and energy costs, and high debt burden and financing costs. Pulp and paper processing does not figure on the 1988 Investment Priorities Plan of the Philippine Department of Trade and Industry but is placed on the list of industrial plants to be rationalised, rehabilitated and/or modernised. In addition, although exports are currently minimal, the pulp and paper industry has been given priority by the Department of Trade and Industry as an industry for exports. Relevant figures for the composition and value of trade in 1988 are provided in *Table 3.2i*.

Table 3.2i *Composition and Value of Pulp and Paper Trade, 1988*

Product	Imports		Exports	
	% of Total Trade	Value (US$ million)	% of Total Trade	Value (US$ million)
Pulp paper, including waste	0.6	56.1	0.2	1.1
Paper and paperboard	1.3	109.5	0.0	1.4
Articles of pulp, paper or paperboard	0.2	15.1	0.0	3.3

Source: UNIDO, 1991

3.2.10 *Sri Lanka*

The pulp and paper industry in Sri Lanka is dominated by the State. The National Paper Corporation is the largest company producing paper products, and had an annual turnover of US$ 14.5 million in 1983/84. Employment by the Corporation during this period was nearly 4600 people.

The composition and value of pulp and paper trade in 1987 is summarised in *Table* 3.2j. As seen from the figures, Sri Lanka relies on imports to bridge the gap between domestic production and demand.

Table 3.2j *Composition and Value of Pulp and Paper Trade, 1987*

Product	Imports		Exports	
	% of Total Trade	Value (US$ million)	% of Total Trade	Value (US$ million)
Pulp paper, including waste	0.3	5.9	0.0	0.0
Paper and paperboard	2.0	40.1	0.0	0.0
Articles of pulp, paper or paperboard	0.3	6.2	0.0	0.4[1]

[1] Rounding errors

Source: UNIDO, 1991

3.2.11 *Thailand*

Although Thailand is a large producer of pulp and paper, it is not self-sufficient, and requires some imports, particularly of paper and paperboard. The general trade situation is summarised in *Table 3.2k*.

Table 3.2k *Composition and Value of Pulp and Paper Trade, 1987*

Product	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Pulp paper, including waste	0.7	87.0	0.1	7.8
Paper and paperboard	1.2	160.3	0.2	25.5
Articles of pulp, paper or paperboard	0.2	21.2	0.2	27.7

Source: UNIDO, 1991

Locally made paper includes Kraft, computer, copier and art paper, as well as corrugated boxes and cartons. Due to forest depletion, there are growing opportunities for timber growers to supply the industry. As a result, the Shell Company of Thailand is among several investors planning to set up eucalyptus plantations.

3.2.12 *Viet Nam*

The pulp and paper industry is an important processor of Vietnam's forestry resources. The industry is largely under the control of the Ministry of Light Industry, and has a total capacity about 200,000 tonnes per year (UNIDO Industrial Development Review Series, 1991). The distribution industry is summarised as follows:

- a large paper mill with a designed capacity of 55,000 tpa built at Bai Bang in the late 1970s/early 1980s in cooperation with the Swedish International Development Authority (SIDA);
- a new mill of French design with a capacity of 48,000 tpa built at Ten Mi in the late 1980s;
- ten old mills operated by the central government with a total capacity of about 40,000 tpa; and
- some provincial enterprises with a combined capacity of 30,000 tpa.

The pulp and paper industry suffers from considerable raw material shortages, and as a result, capacity utilisation rate is only estimated at 50%. These output levels imply a per caput availability of only 3kg of paper per year.

3.3 PRODUCTION AND PROCESSING METHODS

3.3.1 *General*

The principal production and processing methods are shown in *Figure 3.1*.

3.3.2 *Chemical Pulping*

In chemical pulping, cellulose fibres are separated by dissolving lignin and partially dissolving hemicellulose in an aqueous solution of chemicals at elevated temperature and pressure. There are basically two main established technologies:

- *Sulphite pulping* in which wood chips or other lignocellulosic material is digested at 130 to 140 deg C in a solution of calcium bisulphite containing excess sulphur dioxide, or in a solution of sodium, magnesium or ammonium bisulphite with or without excess sulphur dioxide. The advantage of sulphite pulping is the higher brightness and better bleachability of the unbleached pulp when compared with alkaline pulping, and the possibility of by-product manufacture from the pulping waste liquor. However, not all fibrous raw materials can be processed by this method. In addition, the recovery of chemicals is either not possible or too complicated (except with magnesium bisulphite). Only 10 percent of the world chemical pulp production and only 5 percent of the chemical pulp production in developing countries are manufactured by the sulphite processes.

- *Alkaline pulping* in which lignocellulosic materials are digested with aqueous solutions of caustic soda (soda pulping) or caustic soda and sodium sulphide (kraft or sulphate pulping) at 160 to 170 deg C. All lignocellulosic materials can be processed by alkaline pulping. The soda process is especially suitable for agricultural residues and grasses. The recovery of caustic soda and sodium sulphide is a well established process. However when fibrous raw materials with extremely high silica content are used for pulping, chemical recovery is more difficult.

Wood and bamboo are usually digested by the sulphate process. The yield of unbleached pulp is usually in the range of 48 to 52 percent.

Agricultural residues are usually digested by the soda process (without sodium sulphide). The yield is about 50 percent and in the case of rice straw is sometimes as low as 40 percent.

3.3.3 *Washing of Chemical Pulp*

An important operation is the washing of the pulp and extraction of the black liquor containing the dissolved organic substances. Vacuum and pressure driven washers are commonly used.

3.3.4 *Incineration of Black Liquor and Recovery of Chemicals*

The recovery of chemicals from the black liquor of sulphate (kraft) and soda digestion processes is a vital part of the pulping operation as it regenerates chemicals to form fresh digestion liquor. It is also an important environmental protection process.

3.3.5 *Bleaching of Chemical Pulp*

The residual lignin, which was not removed during digestion (cooking), is responsible for the lower brightness of unbleached pulp. Of particular dark colour are sulphate (kraft) and soda pulps. To achieve the required brightness the residual lignin is removed by bleaching.

3.3.6 *Mechanical Pulping*

In mechanical pulping fibres are separated by mechanical action (eg by combined heat, mechanical and mild chemical treatment). The yield is usually higher than 95 percent.

3.3.7 *Paper Making*

Paper making is a physical and hydromechanical process using raw materials which are essentially insoluble in water. Some fibrous material may be dissolved but the amount is marginal, although higher for unbleached pulp.

3.4 *USE/GENERATION OF CHEMICALS*

Chemicals used in the various pulping and paper making processes are listed in *Figure 3.2*.

The total weight of inorganic chemicals used for wood pulping is 420 to 600 kg/t of pulp. About 1000 to 1200 kg of oxygen consuming organic substances are dissolved in the black liquor resulting in a BOD value of 330 to 390 kg/t and COD 1300 to 1500 kg/t of oven dry pulp. The dissolved substances are deeply coloured resulting in a colour load of about 1100 to 1200 kg Pt/t of pulp, and they also contain small amounts of toxic substances such as resin acids and unsaturated fatty acids. Some organic substances are volatile and are contained in the digester and evaporator condensates contributing to the BOD load. During digestion methoxyl groups are split off producing methanol, and are also reacting with sodium sulphide forming odorous compounds such as methylmercaptan, methylsulphide, dimethylsulphide and dimethydisulphide. The amount of total reduced sulphur (TRS) is about 3.5 to 5kg per tonne of pulp.

The chemical charge for pulping agricultural residues is lower but the yield also is lower and this increases the overall BOD. The discharge of TRS (odorous compounds) is negligible as only traces of sulphur are present from water and raw materials.

The black liquor from agricultural residues is less concentrated than that from wood pulping (eg bagasse or wheat straw black liquor is from 8 to 9 percent total solids, and in the case of rice straw it is considerably lower).

Chemicals used for bleaching of chemical pulps include:

- chlorine;

- sodium hypochlorite;

- chlorine dioxide.

A part of chlorinated lignin is difficult to decompose and could have harmful environmental effects.

Bleach effluent has high COD values and is heavily coloured. In conventional bleaching approximately 5 to 7 kg of organically bound chlorine expressed as AOX or TOCl is discharged per tonne of pulp. World wide approximately 250,000 t of organically bound chlorine is discharged from pulp bleaching. Traces of dioxins are also formed in the chlorinated stage.

Use of oxygen pre-bleaching significantly reduces the AOX content as does substitution of elemental chlorine by chlorine dioxide.

The BOD and COD load generated in mechanical pulping is just a fraction of the load generated in chemical pulping but equal to or higher than the total discharge from chemical pulping with recovery. Resins in wastewater from mechanical pumping are toxic. For mechanical pulping without chemicals the BOD values are 15 to 25 kg/t and COD values 25 to 65 kg/t.

A number of inert fillers are used in the paper making process eg china clay, calcium carbonate. Additives such as sizing agents and starches are also used.

The BOD discharge in mechanical waste paper processing is about 15 to 20 kg/t and COD about 40 kg/t of waste paper processed. In de-inking the discharges are about twice as high.

3.5 EMISSIONS AND EFFECTS

3.5.1 *Pulping Processes*

In the pulping process about 50 percent of the lignocellulosic material is dissolved by action of inorganic chemicals generating a biochemical oxygen demand (BOD) load of about 330 to 390 kg per tonne of pulp. In modern pulp mills these dissolved substances are collected by washing of pulp, evaporation, incineration in a recovery furnace, and finally recovery and recycling of inorganic chemicals. The BOD load can be reduced to a value of 10 to 20 kg/t of unbleached pulp before biological treatment.

The current best practicable technology standards in the USA for BOD are 8.05 kg/t of bleached pulp and new source performance standards (NSPS) are 5.5 kg/t of bleached pulp. Old wood based pulp mills with recovery in developing countries still emit up to 40 to 60 kg/t BOD. Activated sludge or aerated lagoon treatment considerably reduces BOD (70 to 90 percent) but is expensive.

Wood pulp mills are using the sulphate process in which odorous gases such as hydrogen sulphide and methylmercaptan are emitted. The amount can be reduced by collecting and burning the gases.

Non-wood mills using agricultural residues use the soda process which is sulphur free and does not emit odourous gases. These mills are facing difficulties in washing of pulp (low capacity of washers) and in recovery of chemicals due to high silica content resulting in scaling which prevents lime reburning. Consequently the recovery efficiency is low and BOD discharges are considerably higher than in modern wood based mills.

Small pulp mills (5 to 30 t/d) often do not have a recovery programme as capital investment for recovery is about 30 percent of total investment. Such mills discharge the total BOD and chemical oxygen demand (COD) load (about 250 to 300 kg BOD/t). However these mills are usually small and the total load on a locality is not that much higher than that of a large capacity modern mill.

3.5.2 *Bleaching Processes*

Bleaching causes increased BOD load and generation of chlorinated organic compounds.

The absorbable organic halides (AOX) load from a conventional bleaching using elementary chlorine and chlorine dioxide is 6 to 8 kg per tonne of pulp. This can be considerably reduced by using oxygen pre-bleaching and substituting chlorine by chlorine dioxide. The AOX load in bleaching of softwood pulp can be reduced to 2 kg per tonne and in bleaching of softwood to 1 kg per tonne taking into consideration that biological treatment reduces AOX by about 40 percent. The future target in developed countries is further replacement of chlorine and reduction of AOX to the range of 0.5 to 1 kg (1995 to 1998) and later from 0.3 to 0.5kg (2000) per tonne.

3.5.3 *Papermaking Processes*

Paper making is mainly a physical and hydromechanical process using raw materials which are nearly insoluble in water. The BOD load is low, but total suspended solids losses (TSS) are higher than in pulping. On a medium level paper machine, the BOD discharge is 2 to 3 kg/t and TSS is 5 to 6 kg/t. With paper machines using waste paper or mechanical pulp the BOD discharges are higher.

Waste paper is an important component of the paper making furnish. The world utilisation rate of waste paper is about 34 percent but in some countries it is up to 50 to 60 percent. Utilisation of waste paper prevents over-cutting of forests. The BOD discharge in waste paper processing is about 15 to 20 kg/t.

Old or second hand paper machines frequently used in developing countries have a BOD discharge of 7 to 15 kg/t and TSS from 35 to 75 kg/t. This is due to water consumption (up to 160 to 200m^3/t of paper), which is very high when compared to that of new paper machines (10 to 20m^3/t).

3.5.4 *Summary of Emissions*

Emissions to aqueous environment, atmosphere and land are summarised in *Figure* 3.2.

(i) *To aqueous environment* - This is the major area of impact of the pulp and paper industry. Large BOD loads are generated by most pulping and paper making processes but these can be minimised by adoption of new processes, modern equipment, or by end of pipe treatment.

(ii) *To land* - Emissions to land are generally not significant, except in the case of non wood based mills with a high silica content. In such cases significant quantities of calcium hydroxide are produced (350 kg $CaCO_3$/t pulp).

(iii) *To atmosphere* - Odorous gases are generated in the sulphate process for making wood pulp, and in the incineration of the black liquors produced in this and other processes. The pollution problem can be overcome by choice of process and by adoption of appropriate treatment.

Figure 3.1 *The Pulp and Paper Industry*

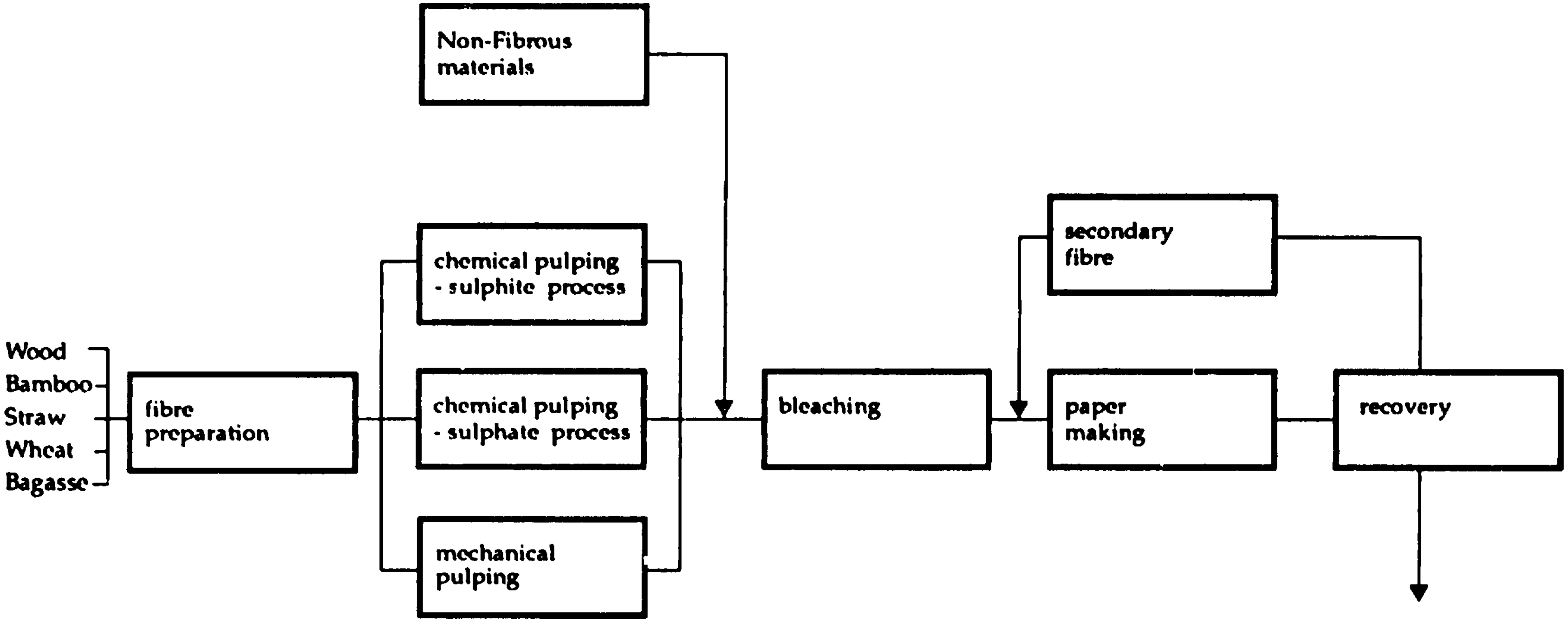
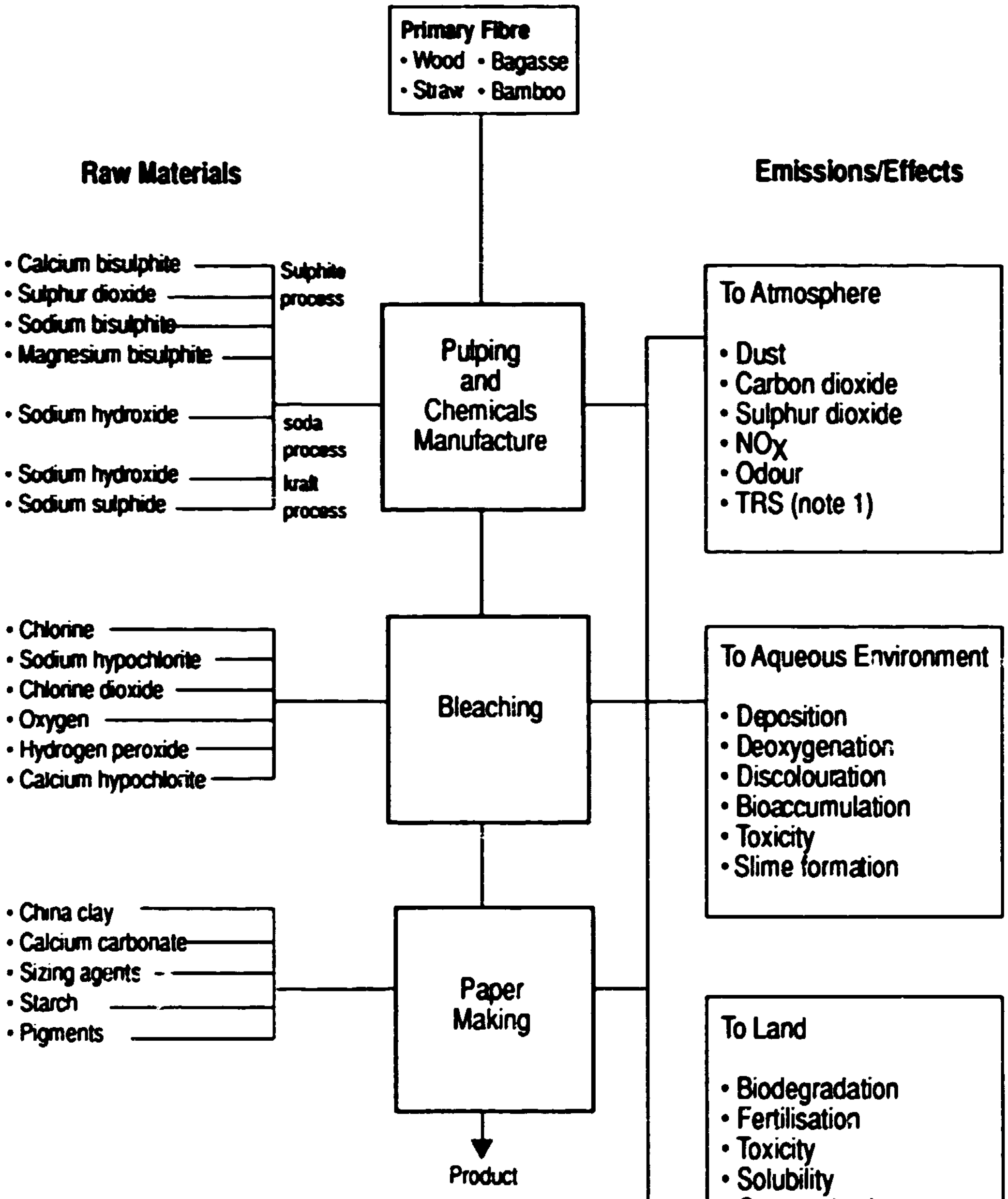


Figure 3.2 *Raw Materials and Emissions The Pulp and Paper Industry*



Note 1: TRS: total reduced sulphur

4 POLLUTION FROM THE PETROCHEMICALS INDUSTRY (PLASTICS) - SOURCES, EMISSIONS AND EFFECTS

4.1 THE INDUSTRY AND THE ENVIRONMENT

The development of synthetic plastics materials undoubtedly has been one of the major technical achievements of the twentieth century. Their growth has been especially impressive since the fifties both in terms of quantity and quality.

Plastics essentially can be divided into:

- thermosetting types in which a heat curing process produces an infusible or insoluble product (by "condensation" polymerisation); and
- thermoplastic types which are characterised by heat softening and cool hardening properties and which are formed by "addition" polymerisation.

The polymerisation processes involved, which are fundamentally different, can be conducted under different reaction conditions and using various catalyst systems. As a result, the molecular weight distribution, structure and properties of the product can be tailored to the subsequent needs of industry and the consumer.

Product polymer powders, granules or liquid resins generally are mixed with a variety of additives to improve durability and properties such as stabilisers, antioxidants, plasticizers, lubricants, pigments or dyes, antistatic additives, flame retardants, reinforcing agents and filters.

Plastics are major products within the petrochemical industry and use up approximately 7 percent of the total consumption of oil and gas.

Thermoplastic products consist of a number of generic groups of polymers of which the polyolefine, low density polyethylene (LDPE), high density polyethylene (HDPE) polyvinyl chloride (PVC), polyacetate (PA) and polypropylene (PP) are the most important.

The principal thermosetting products include phenol formaldehyde resins, urea formaldehyde resins and epoxy resins.

The production of thermoplastics is accompanied by the formation of some by-products such as low molecular weight polymer, reactor residues, crusts and clean outs and wastewater polymer sludge. Most production wastes can readily be recycled. In addition, solvent and plasticizer fumes and monomers can be vented to atmosphere. Overall, the production of thermoplastics is considered to have low environmental impact.

Conversely, the production of thermosetting products has much greater environmental impact due to the generation of waste distillate products, reactor boil outs and bake outs etc.

4.2 THE INDUSTRY IN CONTEXT

4.2.1 *Bangladesh*

Bangladesh's manufacturing sector remains small and narrowly based, with most of it depending on the processing of domestically produced agricultural raw materials. As a result, the plastics industry is comparatively small.

There is little information available on the size of the petrochemicals (plastics) industry in Bangladesh. There is only one oil refinery, Eastern Refining Ltd at Chittagong, which has a maximum demonstrated output of 1.2 million tonnes. It would appear that production of plastic products, the value of which has increased from TK 78 million in 1983/84 to TK 224 million in 1987/88 (accounting for only 0.2% of total industrial production), is primarily dependent on raw material imports.

4.2.2 *China*

China has a newly emerging petrochemical industry which is achieving significant strides in capacity expansion and production. Manufacture of plastics has increased from 916000 tonnes in 1981 to 2196000 tonnes in 1990, and is expected to continue despite gluts in the world market. Total exports of plastics, cellulose and artificial resins were worth US$ 145.5 million in 1989, with nearly 70% of exports to developing countries.

Most enterprises are under the China Petrochemical Corporation. Although the Corporation has forged ahead with the reform of technical systems and extensively integrated scientific research, many petrochemical plants are in need of renovation. The major petroleum-routed synthetic resins produced by the China Petrochemical Corporation are polyethylene, polypropylene and polystyrene. In synthetic resins and plastics, the primary route for manufacture of polyvinyl chloride (PVC) is acetylene chlorination.

Shanghai is a major centre of China's chemical industry, and was producing 15% of the total plastics output in the late 1980s. In recent years it has stagnated in comparison to the neighbouring Jiangsu province and new economic zones, primarily due to the age of equipment. Aside from the age of industrial plants, further factors hampering the expansion of plastics manufacture are infrastructural problems with transportation and energy supplies. These areas will require substantial investment in future years.

4.2.3 *India*

The petrochemical industry in India is of relatively recent origin. In the early 1970s progress was not noteworthy due to only a small number of private sector firms producing polyvinyl chloride, polyethylene, phenol and other items, using mainly naphtha as feedstock. After the advent of the Indian Petrochemicals Corporation Limited (IPCL) in the public sector, and growth in other directions, progress in the 1980s has been quite substantial.

Six new petrochemical complexes are being planned in different centres in the country, with feedstocks of naphtha and gas coming from indigenous sources. Ethylene, the basic raw material for plastics and other items, is in short supply, and as a result the construction of a new plant is being contemplated in Madras. Plans include the establishment of a huge cracker based on naphtha or gas, with import of naphtha of desired quality and partial export of finished products.

The assumed range of expansion to the year 2000 is illustrated in *Table 4.2a*. The assumption of continued rapid growth could become unstuck however, due to two factors:

- production estimates are higher than available demand projections;

- production is based on the availability of naphtha surpluses which may not materialise if the programme of building refineries is delayed.

Table 4.2a *Output of Major Plastic Products and Intermediates*

	Product ('000 tonnes)		
Year	**PVC**	**High-density Polyethylene**	**Low density Polyethylene**
1950/51	NDA	NDA	NDA
1960/61	NDA	NDA	NDA
1968/69	23	Combined high and low density; 25	
1978/79	55	28	58
1984/85 output	84	39	107
1989/90 target	233	125	186
1999/2000 target	455	235	490
Av. annual growth rate (1984/85 - 1989/90)	22.6	26.3	11.7

Source: The Economist Intelligence Unit, 1986.

4.2.4 *Indonesia*

Published statistics show that production of polystyrene and polyvinylchloride was approximately equal to consumption. In the cases of polypropylene and the polyethylenes, consumption was largely met by imports.

4.2.5 *Iran*

Statistics presently show little production of petrochemicals, the national consumption being met by imports.

4.2.6 *The Republic of Korea*

Published statistics show that the production of high- and low-density polyethylene, polypropylene, polystyrene and polyvinylchloride approximated the national consumption, and was of the same order of magnitude as that of the Republic of China, (except in the cases of polystyrene and polypropylene where it was considerably greater).

4.2.7 *Malaysia*

The plastics industry in Malaysia is relatively young and accounted for 3.2% of the output of Malaysia's chemical industry in 1986. There are about 600 local plastic manufacturers with a total turnover of M$ 800 million. Approximately 300 are members of the Malaysian Plastic Manufacturers' Association, and these members account for roughly 80% of the turnover. Most of the manufacturers are located in the more developed states of Selangor, Penang (Butterworth) and Johore. The plastics industry is characterised by small to medium-sized establishments that are family owned.

Imports of plastics and resins accounted for 23.4% of total chemical imports in 1986. This was due to increased demand by plastic fabricators in the manufacture of components and parts for the electrical, electronic and automobile industries. Malaysia's major source of resins are two Singapore-based producers, Phillips Petroleum Singapore and The Polyolefin Company (TPC), which supply half of the 150000 tonnes per annum consumed locally. Malaysia also imports resins from Japan, Taiwan Province, Saudi Arabia, Poland, Canada and the US.

4.2.8 *Pakistan*

From UNIDO figures (1988), imports of plastics, cellulose and artificial resins represented 2.8% of total trade (at US$ 184 million), and exports represented 0.1%.

As most petroleum refining is undertaken in the Sind and Punjab regions, with respective outputs of RS 16740 million and RS 4654 million, it is assumed that any petrochemical manufacture would have a similar geographical distribution.

4.2.9 *The Philippines*

In 1987, the plastics industry in The Philippines comprised of about 400 companies ranging from small, one-machine operations to relatively large operations. Most companies employ 6-10 machines and can be classified as small to medium converters. In 1980, the export value of plastics, cellulose and artificial resins was US$ 31.7 million, with the destination of most exports being developing countries.

Local firms manufacture resin raw material for plastic processing and fabrication, polymeric resins such as polyvinyl chloride, polystyrene and polyamides, and thermosetting resins such as phenolics, alkyds and polyester. All other plastic resins and compounds are imported from industrialised countries.

A number of local bottle-necks are providing some barriers to further expansion, particularly in the lucrative toy industry. These problems include communication difficulties, infrastructure, high power costs, inadequate supply of good quality raw materials and high taxation.

4.2.10 *Sri Lanka*

Sri Lanka is an energy-deficit country which imports around 75% of its energy requirements. Petroleum products are almost exclusively imported, rather than manufactured indigenously, and in 1987 import of plastics, cellulose and artificial resins accounted for 2.3% of total trade with a value of US$ 45.5 million.

4.2.11 *Thailand*

Thailand's plastic industry has grown significantly over the past two decades, and there are now over 2,000 factories involved in producing plastic products. These factories are supplied by six major producers of plastic resin.

The plastics industry is set to benefit from the development of the National Petrochemical complex, which is a major element of the Eastern Seaboard Development. This development will supply the demands of some 1,400 plastic processing companies in and around Bangkok.

In addition, a number of companies undertake plastic foam moulding. The Bangkok Foam Co Ltd, a joint venture with a Japanese company, was among the first to commence manufacture of polyurethane foam. A number of alternative products include flexible, moulded and rigid foams.

4.2.12 *Viet Nam*

The downstream oil processing industry is relatively small in Vietnam. However, following the signing of numerous exploration agreements with foreign oil companies during the past three years, the oil industry is expected to expand in the future. As naphtha and ethylene feedstocks become more abundant, petrochemicals development may follow.

Vietnam anticipates a substantial increase in demand for petroleum products. In addition, the prospect of increased foreign exchange earnings generated by exports of refined products rather than crude oil also represents a major argument in favour of the establishment of a domestic refining industry to add value to the country's oil production.

Major constraints on future development of a plastics industry include:

- lack of the capital and manpower needed to build and operate petrochemical complexes;
- lack of sufficient infrastructure;
- the need to assess the economic feasibility of such large-scale capital investment in order to make optimal use of Vietnam's scarce financial resources.

4.3 PRODUCTION AND PROCESSING METHODS

4.3.1 *Thermoplastic Products*

Thermoplastic products are manufactured by addition polymerisation and are characterised by heat softening, cool hardening properties.

The principal products and production methods include:

- high pressure processing to produce LDPE (used mainly for plastic films) from ethylene feedstock and using a catalyst such as peroxide; the reaction taking place in solution with high pressure separation to recover and recycle unconverted ethylene.
- low pressure processing to produce HDPE (used mainly for blow-moulded containers and injection-moulded articles and pipe) from ethylene feedstock and either butene, octene or hexene co-monomer; the reaction typically taking place in the gas phase in a fluidised bed already containing granular polyethylene polymer with removal of product as dry, free flowing granules from the bottom of the reactor via a gas-lock chamber;
- manufacture of PP by one of several processes similar to those used for polyethylene, the catalysed reactions taking place from solution polymerisation, hydrocarbon slurry polymerisation, polypropylene slurry polymerisation or in the gas phase depending on technology used.
- manufacture of PVA from a benzene solution of vinyl acetate after removal of solvent and unchanged vinyl acetate;
- manufacture of PVC from a suspension of vinyl chloride in water with recovery of PVC particles by spray drying or coagulation by acid addition;

Composite flow diagrams of typical process steps for LDPE and PVC production are shown in *Figure 4.1*.

4.3.2 *Thermosetting Products*

Thermosetting products are manufactured by condensation polymerisation. The product obtained depends primarily on the concentration and chemical nature of the reactants, the nature and concentration of the catalyst used, the temperature and reaction time and the modifying agents, fillers and extenders.

Manufacturing is carried out in batch reactors followed by water cooled cooling trays, blending units, dryer units, grinders and granulators as appropriate. During condensation in the batch reactor, reaction water is eliminated and forms the upper of two layers. This is generally removed under vacuum without addition of heat. A typical unit operation sequence for production of phenol-formaldehyde resins is also shown on *Figure 4.1*.

4.4 USE/GENERATION OF CHEMICALS

A limited number of chemicals are used in the manufacture of thermoplastic and thermosetting plastic materials, the principal chemical groups being listed in *Figure* 4.2.

In the manufacture of thermoplastic materials, most chemicals used are consumed in the production process or produced in a form which permits successful recycling. Some unreacted monomer may be discharged as waste.

A wide range of polymerisation catalysts are used and many have to be extracted, neutralised and discharged as waste when spent.

In the manufacture of thermosetting materials however there can be significant loss of raw materials to waste.

4.5 EMISSIONS AND EFFECTS

4.5.1 Emissions to Aqueous Environment

Potential emissions to aqueous environment include:

- unreacted monomer from thermoplastic reactions;
- distillate fractions containing unreacted raw materials and intermediate reaction products from thermosetting product manufacture;
- reactor boil outs or bake outs carried out periodically to remove deposits formed on the walls of polymerisation vessels and associated equipment;
- aqueous phase discharges from recovery condensers material;
- aqueous phase discharges from fume scrubbing equipment;
- contaminated steam condensates;
- contaminated cooling waters;
- water treatment plant regeneration liquors;
- contaminated discharges containing lubricating oil from compressors.

The significance of aqueous emissions from plastics manufacture ranges from minimal, eg from LDPE/HDPE manufacture to very significant, eg distillate fraction discharges from thermosetting product manufacture.

Typical pollution loads per tonne of product arising from phenolic resin production (as solid) and assuming free phenol concentrations of 5 percent and 1 percent in the product resin are detailed in *Table 4.5a* below.

Table 4.5a *Pollution Loads from Phenol-Formaldehyde Resin Manufacture*

	Product at 1% Free Phenol	Product at 5% Free Phenol
Volume (m^3/t)	0.5	0.6
Phenol (kg/t)	18	58
Formaldehyde (kg/t)	4	5
COD (kg/t)	165	215

Source: UK manufacturers of phenol-formaldehyde resins

Typical characteristics of a combined aqueous discharge from a 60 t/d facility manufacturing a range of phenolic resins (solids and liquids) in addition to urea formaldehyde/melamine resins is provided in *Table 4.5b*.

Table 4.5b *Wastewater Characteristics - Mixed Thermosetting Resin Production (60 t/d)*

Parameter	Value
Volume (m^3/d)	200
Phenol load (kg/d)	1,275
Phenol concentration (mg/l)	6,375
Formaldehyde load (kg/d)	175
Formaldehyde concentration (mg/l)	875
COD load (kg/d)	5,200
COD concentration (mg/l)	26,000

Source: UK manufacturer

Many methods have been devised for the destruction/treatment of wastewaters containing phenols and formaldehydes. These include:

- biological processes;
- phenol recovery through solvent extraction;
- chemical oxidation;
- adsorption processes;
- wet oxidation;
- incineration.

It is natural to think first of biological treatment as a means of purifying wastewaters of the strength noted in *Table 4.5b* since it is well established that the two principal impurities can be aerobically biologically degraded under appropriate conditions. Where this route is adopted it is usually the most economical method. However, for successful biological treatment it is necessary to adopt a uniformly mixed suspended growth type plant to ensure "dilution" of the incoming feed. This is due to batch test results showing phenol to be toxic to micro organisms at concentrations above a few hundred mg/l.

4.5.2 *Emissions to Land*

Potential emissions to land from primary production processes include:

- reactor bottoms or tars eg from PVC production;
- spent catalyst materials;
- off grade products;
- extrusion purgings, chunks or fine particles;
- floor sweepings, scrap paper etc;
- wastewater treatment plant sludges eg surplus sludge from suspended growth biological reactors (for treatment of aqueous emissions containing significant quantities of phenol, formaldehyde, methanol etc).

The more significant impacts arise from the disposal of reactor "tars" and spent catalyst materials and considerable care is required to ensure appropriate extraction and "neutralisation" prior to disposal. Appropriate disposal procedures for reactor "tars" include incineration.

A second category of wastes arises from secondary production processes, namely the conversion of plastic raw materials into semi finished or finished products. They consist of trimming, distorted and incomplete products, surpluses, products rejected during quality control and material arising during the starting up or shutting down of the plant.

However, provided such waste is carefully segregated at source according to its nature, colour and additives, recovery by recycle is generally a viable proposition. Even smaller firms can no longer afford to waste these raw materials.

It should be noted that direct recycling is sometimes not desirable or possible because the material is polluted or is comprised of composite components, or specialist equipment is required which cannot be justified economically.

4.5.3 *Emissions to Atmosphere*

Potential emissions to atmosphere include:

- solvents, plasticizer fumes and monomers arising from thermoplastics manufacture;

- phenol and formaldehyde fumes arising from thermosetting materials manufacture, also from the drying or curing of resins or laminate assemblies;

- polymer dust arising from crushing and grinding operations.

A number of these emissions are potentially toxic or carcinogenic, eg the vinyl chloride monomer.

Scrubbing with aqueous medium often is carried out for appropriate discharges, as is direct incineration. However, wherever possible emissions, particularly from thermoplastics manufacture, are led to either recovery facilities or to flare stacks for smokeless burning rather than being directly emitted to atmosphere.

Cyclone separators and bag filters are generally installed to remove polymer fines from the exhausts of pellet transfer system air.

Figure 4.1 *The Petrochemicals Industry (Plastics)*

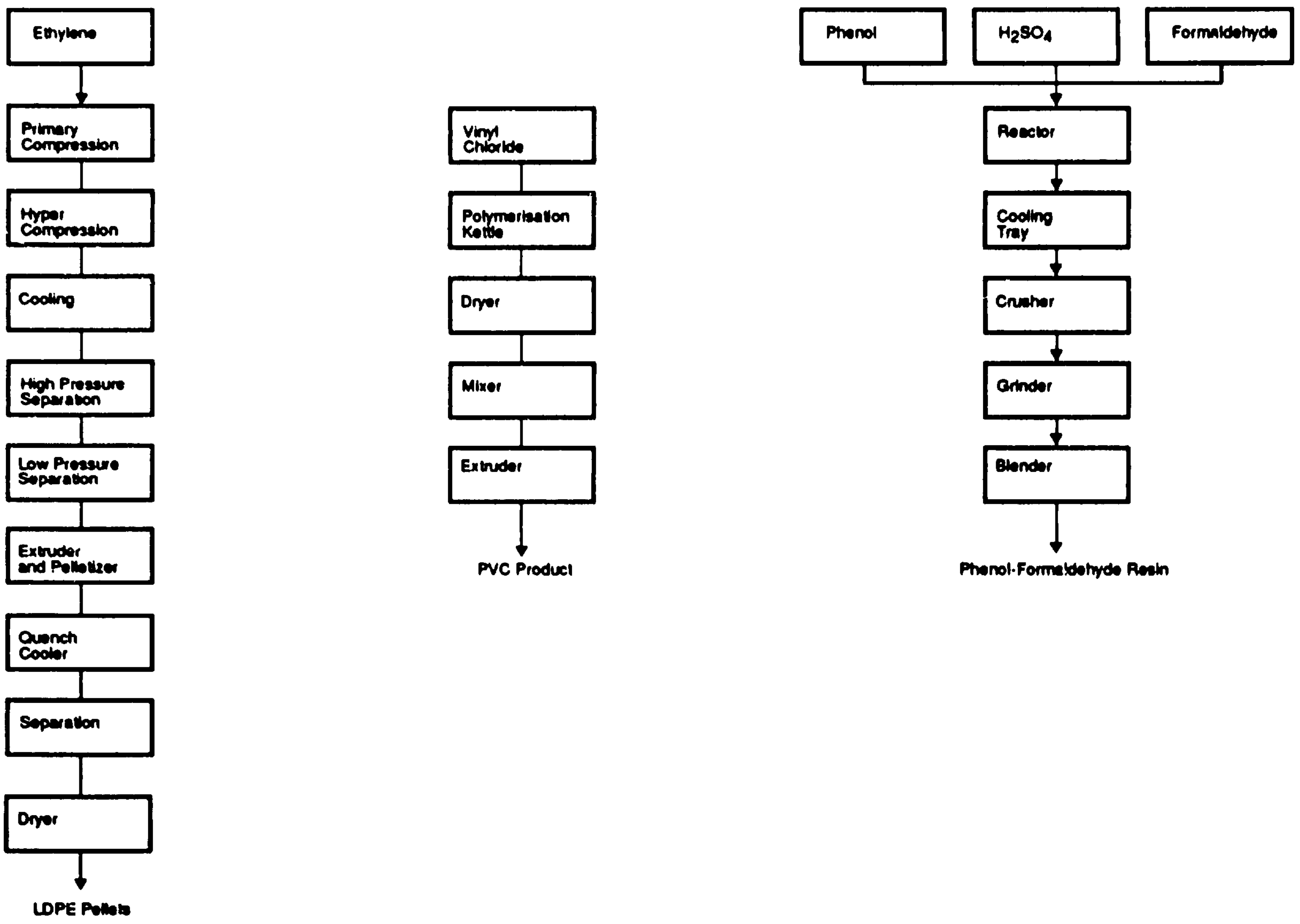
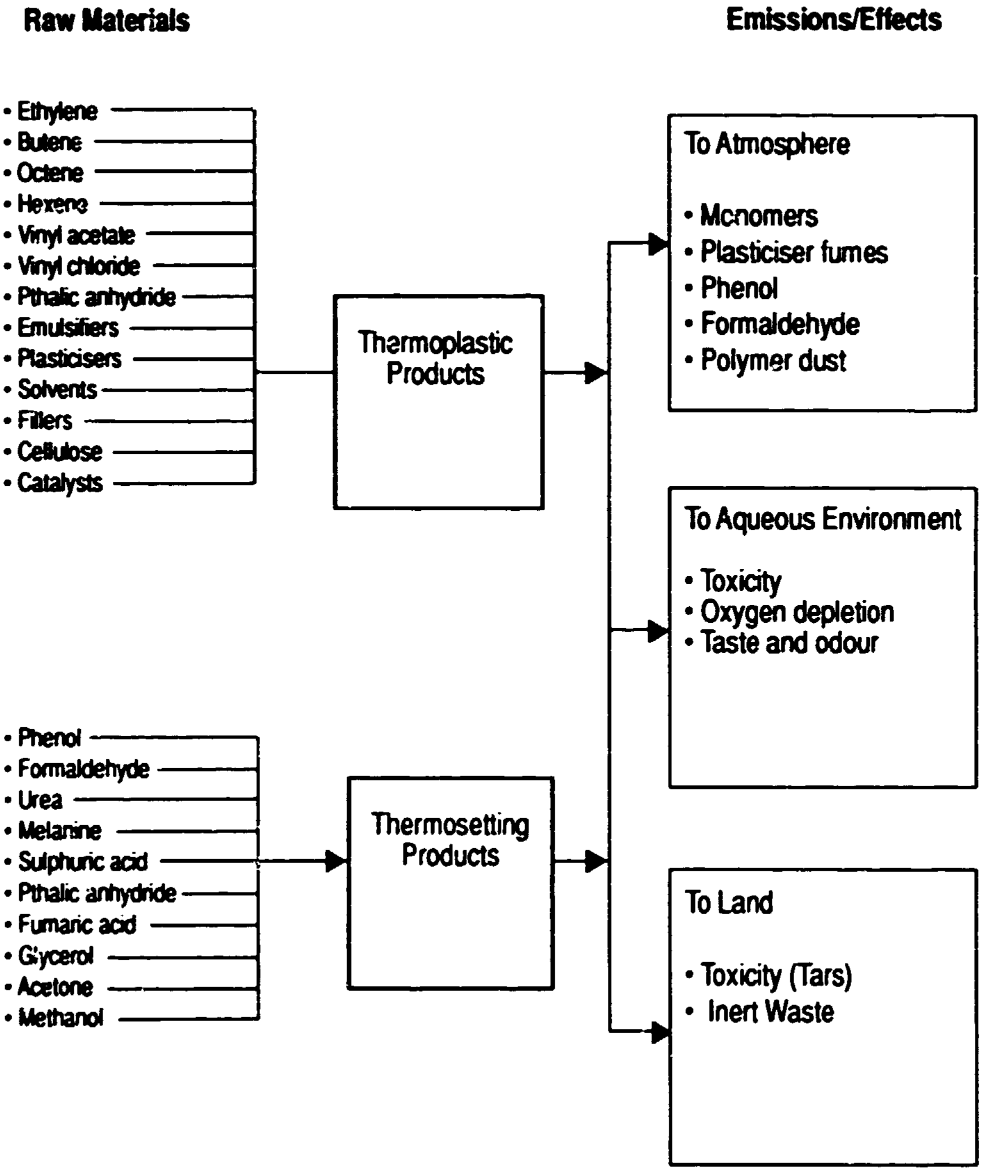


Figure 4.2 ***Raw Materials and Emissions***
The Petrochemicals Industry (Plastics)



5 POLLUTION FROM AGROCHEMICALS (FERTILIZERS AND PESTICIDES) INDUSTRY - SOURCES, EMISSIONS AND EFFECTS

5.1 THE INDUSTRY AND THE ENVIRONMENT

5.1.1 *Fertilizers*

Fertilizer manufacturing processes vary between plants; there are four principal product groups:

- nitrogen-based fertilizers;
- phosphate-based fertilizers;
- potassium based fertilizers;
- ammonium phosphate and mixed nitrogen/phosphate/potassium based (NPK) fertilizers.

In general, liquid, gaseous and solid waste emissions from fertilizer manufacture include:

- sulphur dioxide (SO_2)
- oxides of nitrogen (NO_x)
- acids and alkalies
- ammonia
- urea
- arsenic
- methanol
- hydrogen sulphide
- fluoride
- phosphates
- toxic metals
- phospho-gypsum
- untreated phosphate rock

The degree of potential environmental impact is both process-specific and site-specific, but overall can reach significant levels.

5.1.2 *Pesticides*

Pesticides manufacturing is a specialised sector of the chemical industry. It is characterised by a rather large number of products of very diverse chemistry. Products tend to appear and disappear from the market for various reasons and often there may not be time to maximise the efficiency of the production processes before the product is withdrawn. Few companies are engaged solely in the production of pesticides.

The formulation of pesticides into specialised products for supply to the consumer is often separate from manufacturing and may be organised on a regional basis.

The main classes of products are as follows:

- Insecticides
    - Organochlorine
    - Organophosphate
    - Carbamate

- Herbicides

- Fungicides

- Others (growth regulators etc)

Methods of production are typical of small to medium scale industrial synthesis starting from simple organic and inorganic reagents. Manufacturing is almost exclusively based on batch operations.

Waste emissions contain unreacted starting materials, product, by-products, organic and mineral acids, solvents etc. In some cases toxic inorganic substances such as arsenic and mercury may be present.

5.2 THE INDUSTRY IN CONTEXT

5.2.1 *Bangladesh*

Bangladesh's chemicals industry is expanding due to the presence of natural gas. Whilst most fertiliser demand was previously met by imports, output within Bangladesh has almost doubled since 1980/81, to reach 1,621,000 tonnes by 1989/90. The country is now self-sufficient in nitrogenous fertilisers (produced in the form of urea), but remains heavily import dependent as far as the supply of phosphate, potassic and compound fertilisers is concerned.

The composition and value of fertiliser trade is summarised in *Table 5.2a*.

Table 5.2a *The Composition and Value of Fertiliser Trade in 1987*

Fertiliser	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Nitrogenous	0.0	0.0	0.2	2.4
Phosphatic	1.2	30.4	0.0	0.0
Potassic	0.4	10.7	0.0	0.0

Source: UNIDO, 1991

There are five fertiliser plants in the country - Chittagong Urea Fertiliser, Zia Fertiliser, Ghorashal Urea Fertiliser, Fechuganj Factory and Potash Urea plant. Two more fertiliser plants are in the pipeline, namely;

- Jamuna fertiliser plant which is expected to come into operation by the end of 1991 and will be the largest ammonia-urea complex in the country;
- a fertiliser plant at Chittagong in a joint venture with Italian and Japanese firms.

Most factories in Bangladesh are operating below capacity due to factors such as unsatisfactory construction and installation of plant machinery, poor maintenance, loss of skilled personnel, power failures and poor management. In order to expand the productive base of the Bangladesh fertiliser industry in future years, it will become increasing important to investigate alternative technology spectrums for the production of fertilisers on a small scale.

5.2.2 *China*

China is endowed with an abundant raw material resource base for the manufacture of acid and soda, and chemical fertilisers such as nitrogenous compounds, phosphate and potash. Priority has been accorded (during the Seventh Plan, 1986-1990) to the rapid growth of compound fertiliser production, and to the expansion of production of fine chemicals such as pesticides.

Output of chemical fertilisers (nitrogenous and phosphate) has increased from 12.4 million tonnes in 1981 to 187.9 million tonnes in 1990. Although a decline in production occurred in 1985 due to the government's decision to close around 200 small inefficient plants producing low quality products, China has continued to expand the production capacity of high grade fertilisers, particularly phosphates. In the mid 1980s around 17% of apparent consumption of chemical fertilisers was met by imports, but an objective of the government is to reach self-sufficiency by the year 2000.

In contrast to chemical fertilisers, there has been a drastic fall in the production of chemical pesticides over the years. The 1990 output was 229,000 tonnes which was less than half of the 1981 production level. Present demand for high quality pesticides is 25-50% higher than the available supply, and a number of agricultural areas have subsequently suffered from insect damage. For example, some 100 million paulownia trees in the plains of Henan have been partially defoliated by bag worms. With around 30% of the country's arable land being treated with pesticides, China represents one of the largest pesticide markets in the world.

5.2.3 *India*

The agrochemicals industry in India has recently been receiving increasing attention, and is considered an important sector for a variety of reasons:

- as a way to increase agricultural outputs and efficiency;
- as a significant component of the chemical industry;
- as the main consumer of natural gas (fertiliser manufacture).

Both the public and private sectors have formulated and implemented a number of projects over the past four decades, and as a result the installed capacity has increased steadily. To provide an illustration, installed capacity increased from 90000 tonnes of nitrogen and 60000 tonnes of phosphatic fertiliser (BO_5) in 1951/52, to 8.15 million tonnes of nitrogen and 2.65 million tonnes of P_2O_5 in 1988/89.

Based on 1988/89 figures there were 55 large firms producing nitrogenous and complex fertilisers, 84 smaller firms producing single superphosphate and six firms manufacturing ammonium sulphate. Production and consumption figures are shown in *Table 5.2b*. Average capacity utilisation rate for the nitrogenous and phosphatic fertiliser plants ranged between 60 and 80%, primarily due to difficulties related to the old age of public sector plants and the persistent shortage of power. Newer, more efficient plants based on natural gas are being proposed and gradually commissioned.

Table 5.2b *Production and Consumption of Fertilisers, 1971/72-1987/88 (Millions of tonnes)*

	Production			**Consumption**				**Imports**			**Value of imports (million rupees)**
Year	N	P_2O_5	Total	N	P_2O_5	K_20	Total	N	P_2O_5	K_2O	
1970/71	0.83	0.23	1.06	1.49	0.46	0.23	2.18	0.48	0.03	0.12	566.4
1982/83	3.42	0.98	4.40	4.22	1.44	0.73	6.39	0.43	0.06	0.64	2,735.3
1985/86	4.33	1.43	5.76	5.82	2.07	0.85	8.74	1.68	0.82	0.90	14,050.0
1987/88	5.46	1.67	7.13	5.82	2.27	0.92	9.01	0.18	-	0.81	2,237.7

Source: Fertiliser Association of India, *Fertiliser Statistics* (New Delhi), various issues

Simultaneously with increasing fertiliser consumption, the demand for crop protection chemicals has been rising. In 1987/88, there were 47 firms engaged in the manufacture of technical grade pesticides, and over 500 firms making formulations. Capacity was 105,330 tonnes and consumption was 56,920 tonnes. With this rising internal production it has been possible to substantially reduce imports, and special efforts are being made to boost exports in technical grade products.

It should be noted that a decision has been taken by India to remove subsidy from the manufacturing sector. This could have a major impact.

5.2.4 *Indonesia*

An indication of activity in the agrochemicals sector is provided by the trade figures shown in *Table 5.2c* below.

Table 5.2c *The Composition and Value of Trade in Fertilisers, 1989*

	Imports		Exports	
Fertiliser	**% of Total Trade**[1]	**Value (US$ million)**	**% of Total Trade**[1]	**Value (US$ million)**
Nitrogenous	0.0	0.6	0.8	163.4
Phosphatic	0.3	54.6	0.0	0.1
Potassic	0.3	45.9	-	-

[1] There may be some rounding errors

Source: UNIDO, 1991

5.2.5 *Iran*

An indication of the fertiliser industry in Iran is provided via *Table 5.2d* below; the composition and value of trade in 1977.

Table 5.2d *The Composition and Value of Fertiliser Trade in 1977*

Fertiliser	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Nitrogenous	0.2	34.1	-	-
Phosphatic	1.0	4.8	-	-
Potassic	0.0	0.0	0.0	0.0

Source: UNIDO, 1991

5.2.6 *Republic of Korea*

As an indication of activity in this sector, a summary of the composition of value and trade in fertilisers in 1989 is presented in *Table 5.2e*.

Table 5.2e *The Composition and Value of Trade in Fertilisers, 1989*

	Imports		Exports	
Fertiliser	**% of Total Trade[1]**	**Value (US$ million)**	**% of Total Trade[1]**	**Value (US$ million)**
Nitrogenous	0.0	15.7	0.0	25.3
Phosphatic	0.0	1.1	0.0	3.9
Potassic	0.1	79.6	0.0	10.7

[1] There may be some rounding errors

Source: UNIDO, 1991

5.2.7 *Malaysia*

The manufacture of fertilisers and pesticides has increased in value from M$ 489.4 million in 1982 to M$ 680.6 million in 1986. Although the agrochemicals industry is relatively buoyant, its share in the total chemical industry output has suffered a marked decline in the same period.

In the fertiliser subsector, Malaysia has at present one urea production plant, one ammonium nitrate plant, about 10 compound granulated fertiliser plants and about 80 fertiliser mixing plants. Although Malaysia is self-sufficient in nitrogenous fertiliser, it is still completely dependent on imported phosphate and potash. Domestic supply of inorganic chemicals amounts to 25-35% of demand. Malaysia's self-sufficiency in nitrogenous fertiliser stems from the ASEAN Bintulu Plant that came on stream in the mid-1980s, with a production and marketing strategy aimed at the ASEAN region. The plant has an installed capacity of 495,000 tonnes per annum of granular urea, and product from the plant is expected to replace ammonium nitrate as the major nitrogen source in Malaysia due to its low cost advantage.

Domestic demand for fertilisers is expected to grow at a modest annual rate of 4.8% during 1991-1995, a reduction from the estimated 1986-1990 demands of 7.2%. Anticipated growth of pesticides in the same 1991-95 period is somewhat higher at 6.4%.

5.2.8 *Pakistan*

Pakistan currently has nine firms engaged in the production of fertiliser. A large proportion of production is controlled by the public sector company, the National Fertiliser Corporation (NFC), which operates five subsidiaries accounting for 50% of nitrogen capacity and 100% of the country's phosphorous capacity. A further large concern is Hazara Phosphate

Fertiliser Ltd, Haripur, which produces 110 tpd sulphuric acid and 300 tpd of granulated super phosphate fertiliser. Potash requirements are met entirely by imports.

Although capacity has been increasing since the early 1980s, Pakistan continues to depend on imports, as illustrated in *Table 5.2f*.

Table 5.2f ***Composition and Value of Fertiliser Trade in 1988***

Fertiliser	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Nitrogenous	0.0	3.1	0.0	0.0
Phosphatic	2.9	189.1	negligible	0.2
Potassic	0.0	0.0	0.0	0.0

Source: UNIDO, 1991

There are very high levels of capacity utilisation in fertiliser firms, which indicates that existing supply shortages can be alleviated by expanding current production. The government has therefore been encouraging rehabilitation of existing plants, with the views of conserving energy, reducing costs and maximising capacity utilisation.

5.2.9 *The Philippines*

The Filipino agrochemicals sector is relatively small in comparison to manufacture of other goods such as electronics and textiles. UNIDO figures (1988) for the composition and value of trade in the fertiliser subsector are summarised in *Table 5.2g* below.

Table 5.2g ***The Composition and Value of Trade in Fertilisers, 1988***

	Imports		**Exports**	
Fertiliser	**% of Total Trade**	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Nitrogenous	1.2	105.0	0.0	3.5
Phosphatic	0.0	0.8	0.3	19.7
Potassic	0.2	20.0	0.0	0.01

Source: UNIDO, 1991

5.2.10 *Sri Lanka*

The leading fertiliser company is Ceylon Fertiliser Corp, a state-owned enterprise which had an approximate turnover of US$ 14 million in 1983/84 Sri Lanka has not reached self-sufficiency with regard to fertiliser production, and relies on imports from neighbouring developing countries and the EEC.

A summary of the composition and value of fertiliser trade in 1987 in shown in *Table 5.2h*.

Table 5.2h *Composition and Value of Fertiliser Trade In 1987*

Fertiliser	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Nitrogenous	1.2	23.7	0.0	0.0
Phosphatic	0.3	6.7	0.0	0.0
Potassic	0.6	31.8	0.0	0.0

Source: UNIDO, 1991

5.2.11 *Thailand*

An indication of the industry is provided in the value of trade *Table 5.2i* below.

Table 5.2i *The Composition and Value of Fertiliser Trade in 1987*

Fertiliser	**Imports**		**Exports**	
	% of Total Trade	**Value (US$ million)**	**% of Total Trade**	**Value (US$ million)**
Nitrogenous	0.2	27.7	0.0	0.0
Phosphatic	0.0	1.0	0.0	0.0
Potassic	0.0	9.5	-	-

Source: UNIDO, 1991

5.2.12 *Viet Nam*

Figures from UNIDO (Industrial Development Review Series, 1991) although variable, indicate that Vietnam is gradually expanding its production of fertilisers, thereby reducing overall import demands. This trend is illustrated in *Table 5.2j*.

Table 5.2j *Fertiliser Imports for the Period 1983-1989*

Year	Imported Amount ('000 tonnes)
1983	1200
1984	1600
1985	1500
1986	2059
1987	1567
1988	1999
1989	1472

Source: UNIDO, 1991

The differences in the historical evolution of northern and southern Vietnam have resulted in significant variations in regional industrialisation patterns. Greater emphasis has been placed on the development of a manufacturing industry in northern Vietnam, an emphasis which was reinforced during the period of partition, when orthodox communist strategies aimed at the establishment of a heavy industrial base were pursued. As a result, the northern part of the country accounts for the bulk of the country's fertiliser manufacture.

5.3 PRODUCTION AND PROCESSING METHODS

5.3.1 General

The principal product lines for manufacture of fertilizers are shown on *Figure 5.1*. Principal product lines for pesticides are shown in *Figure 5.2*.

5.3.2 Nitrogen-Based Fertilizers

The most common nitrogenous fertilizers are ammonium nitrate and urea. Ammonia is produced from the reaction of nitrogen with hydrogen. Ammonium nitrate is made by neutralising ammonia with nitric acid; the product being in liquid or solid form (pellets or prills). Ammonium sulphate is produced by reacting sulphuric acid with ammonia or by reacting calcium sulphate with ammonium carbonate.

Nitric acid is produced in many fertilizer plants by the oxidation of ammonia. Urea is manufactured by the reaction of ammonia with carbon dioxide to form ammonium carbamate, which is subsequently dehydrated to urea. Urea is commonly made at the same plant as ammonia fertilizer.

5.3.3 Phosphate-Based Fertilizers

Phosphate fertilizers are produced by reacting phosphate rock with sulphuric acid (super phosphate) or phosphoric acid (triple superphosphate).

The most common phosphate fertilizers are normal superphosphate (SSP) and triple superphosphate (TSP). The basic manufacturing processes involve sulphuric acid production, phosphate rock grinding, wet process phosphoric acid production, concentration and clarification, and normal and triple superphosphate preparation.

For every tonne of phosphate rock used, about 1.5 tonnes of phosphogypsum are produced as a by-product. The phosphogypsum contains impurities, particularly phosphates, fluorides, toxic metals and trace amounts of certain radionuclides, especially radium 226. The quantity of these impurities depends on the phosphoric acid process employed, plant operational procedures and the phosphate rock quality.

Sulphuric acid is made at phosphate fertilizer plants from sulphur, air and water. Nitric acid or hydrochloric acid may also be used. Sulphuric acid is reacted with ground phosphate rock to produce normal superphosphate (SSP). The initial slurry is discharged onto a slow moving conveyor and transported to a den where it solidifies and is then cured in storage for two to four weeks before leaving the plant. The use of phosphoric instead of sulphuric acid produces triple superphosphate (TSP). The initial TSP product is also a slurry which solidifies and is then cured in the same way to allow the completion of the chemical reactions.

5.3.4 *Ammonium Phosphate and Mixed Fertilizers*

Ammonia and phosphoric acid are reacted to form either monoammonium or diamonium phosphate. Ammonium phosphate is usually produced at the same site as phosphate-based fertilizers. The final granular product is dried and cooled before leaving the plant.

Potash fertilizers are produced from the mineral sylvite.

Mixed fertilizers are produced by combining straight fertilizers in the required ratios.

Granular compound fertilizers are produced in a two-stage process;

- the wet stage which involves a reactor and neutraliser;
- the dry stage which involves granulation.

5.3.5 *Pesticides*

Typical inorganic and organic pesticides can be characterised under the following headings:

- *Herbicides*
  - Triazines such as Actrazine
  - Amides such as Alachlor

    - Diphenyl Ether herbicides
    - Carbamate herbicides such as Thio bencarb
    - Urea herbicides such as Linuron
    - Hormone herbicides such as 2, 4 - D, MCPA.
- *Insecticides*
    - Organo phosphate insecticides such as Methyl parathion
    - Carbamate insecticides such as Carbofuran
    - Organo chlorine insecticides such as Endrin, Heptachlor
- *Fungicides*
    - Benzimidazole fungicides such as Carb endazin
    - Organo phosphorus fungicides such as Katazen-P and Hinosan
    - Organic compounds including substituted thiocarbamates.

Methods of production are typical of small to medium scale batch industrial synthesis. Compounds are produced in a variety of formulations including suspension, emulsions, "wettable" powders, granules, dusts, miscible oils, aerosols, solutions, soluble concentrates etc.

Acids are normally formulated either as ester or solution of the amine, sodium or potassium salt; frequently two or more compounds are blended in formulations.

The range of compounds covered by the industry is therefore very large, as is the number of different formulation of products marketed.

Identification of individual production and processing methods is not relevant in this case. What is more relevant is detailed assessment of batch chemical processing techniques with emphasis on the attainment of optimum yield performance and thereby to:

- minimise generation of aqueous emissions;
- avoid atmospheric pollution;
- minimise generation of solid waste material including liquid concentrates as distinct from effluents.

5.4 USE/GENERATION OF CHEMICALS

5.4.1 Fertilizers

Chemicals typically in use and generated in the agrochemicals (fertilizers) industry are listed in *Figure* 5.2.

5.5 EMISSIONS AND EFFECTS

5.5.1 Nitrogen based Fertilizers

Aqueous emissions from the nitrogen based fertilizer industry include:

- general site effluents containing nitrogen (as ammonia, nitrate or organic nitrogen), dissolved and suspended solids, acids and alkalies;

- steam condensate effluent containing ammonia (from ammonia manufacture);

- waste stream containing carbon dioxide, ammonium carbamate and urea (from urea manufacture). Most of these can be recycled to the manufacturing process including urea after hydrolysis. (Wastewater discharge is usually unlikely since most urea plants have a negative water balance);

- wastewaters from oxidation of ammonia (from nitric acid manufacture) although, because the overall process has a negative water balance, actual losses arise through spills and leaks only.

In relation to emissions to atmosphere it should be noted that:

- NO_x may be released from urea prilling towers at concentrations of 500-1000 mg/m^3. These fumes may be extracted by wet scrubbers or electrostatic precipitators.

- NO_x emissions from nitric acid manufacture are commonly in the range 1,000-10,000 mg/m^3. However such emissions can be reduced by 90-95 percent by catalytic conversion with ammonia to reduce NO_x to N_2.

- Neutralisation of nitric acid by ammonia (manufacture of ammonium nitrate), gives off vapour containing nitrogen compounds. Prilling towers also emit ammonium nitrate fumes which form around dust particles. This dust can be removed prior to gas release and the nitrogen eliminated by biological oxidation.

In relation to emissions to land, arsenic trioxide sludge is produced when CO_2 is eliminated during ammonia manufacture. Diatomaceous earth used as a sulphur filter contains up to 50 percent sulphur. The vanadium catalyst used in sulphuric acid manufacture requires safe disposal in view of the high toxicity of vanadium compounds.

5.5.2 *Phosphate Based Fertilizers*

Phosphoric acid is the major intermediate used to produce phosphate fertilizer. Approximately 70 percent of all fertilizer P_2O_5 is derived directly from wet-process phosphoric acid. Most of the balance is derived from phosphate concentrate that is usually treated with phosphoric or other acids (sulphuric or nitric acid) to increase its solubility.

The degree of potential environmental impacts are process and site specific. The main possibilities include the following:

- Disturbance of land used for phosphogypsum and contaminated process water storage.
- Contamination of water resources caused by the disposal of phosphogypsum and its associated process water, including acidity, dissolved metals, and radionuclides.
- Fluorine emissions to the atmosphere from the phosphoric acid process.
- Escape of radionuclides that may be harmful to human health.
- Airborne solid and liquid particulates including those caused by wind erosion of phosphogypsum stacks.
- Release of contaminated cooling water, plant site stormwater drainage, and boiler blowdown residue.
- Release of metals and other residues from the regeneration or disposal of spent catalyst from sulphuric acid production units.
- Release of solvents, oils and other contaminants from plant maintenance and workshop activities.

The major problem associated with phosphate fertilizer plants is the production of the solid waste phosphogypsum. About 3 tonnes of phosphogypsum are produced for every 2 tonnes of phosphate rock processed. it is usually discharged to the sea or to settlement ponds. If discharged to settlement ponds the pond water contains phosphate (6,000-12,000 mg/l), fluorine (3,000-5,000 mg/l), silica (2,000 mg/l), calcium (350-1,200 mg/l), sulphate (2,000-4,000 mg/l), sodium (1,700 mg/l), potassium (300 mg/l), ammonia (0-100 mg/l) and nitrate (0-100 mg/l), and is acidic (pH 1.0-1.5).

The grinding of phosphate rock and fertilizer granulation generates large quantities of dust. Even the best emission control systems will not eradicate all particulate emissions. Cooling waters in phosphate fertiliser plants generally contain phosphorus, fluorine and chlorine and may be reused to scrub gases. It can then be used to slurry the gypsum into settlement ponds.

In super phosphate manufacture, 25 percent of the fluorine present may be released as SiF_4. In triple phosphate manufacture less fluorine is produced. Scrubbing will produce an effluent containing hydrogen fluoride and phosphate as well as silicon tetrafluoride: P(340 mg/l) and F(1,100 mg/l).

In ammonium phosphate production NO_x and fluorine containing gases are the main gaseous emissions produced. NO_x can be removed by catalytic reduction. Water scrubbing of gaseous emissions generates an effluent containing 25-250 mg/l fluorine.

In the production of mono or di ammonium phosphate, ammonia is the main gaseous effluent.

In sulphuric acid manufacture the production of sulphurous emissions and mists is an environmental concern. A typical 500 tonne per day (tpd) plant discharges about 6.5 tpd SO_2, equivalent to an hour's discharge from a 200 MW power station burning heavy fuel oil.

5.5.3 *Effects of Emissions*

(i) Atmospheric pollution

The primary air pollution problems are caused by emissions of gaseous compounds of sulphur, nitrogen and fluorine and emissions of particulate matter. Both SO_2 and NO_x have local and long-range environmental impacts.

High concentrations of SO_2, particularly when associated with particulates, are liable to cause respiratory problems amongst the local population, especially in individuals predisposed to pulmonary illness.

NO_2 emissions can contribute to the formulation of photochemical smog and ozone in the lower atmosphere. These have adverse impacts on human health and agricultural productivity. NO_x itself causes respiratory irritation at high concentrations.

The long-range transportation of SO_2 and NO_x can lead to acid precipitation, either as acid rain, snow or mist and has been linked to declining forest, agricultural and aquatic ecosystem productivity in north America, northern Europe and China.

Localised high concentration of fluorides can lead to symptoms of fluorosis amongst the resident population and, at lower concentrations, fluoride can cause injury to vegetation and, indirectly, to herbivorous animals.

Irritation to the mucous membranes of the nose, throat and eyes results from the alkaline properties of ammonia at concentrations in excess of 35 mg/m^3. This is also its odour threshold.

(ii) Surface water pollution

The introduction of excess plant nutrients such as ammonia, urea and phosphates into aquatic ecosystems causes enrichment ('eutrophication') of streams, rivers and lakes causing excessive growth of micro-organisms and plants which can lead to deoxygenation of the water and animal death.

The disposal of phosphogypsum and other solid waste into rivers and coastal waters has adverse effects on aquatic organisms. This is mainly due to the fine solids which by interfering with feeding and breathing have led to the disappearance of shrimp, lobster and filter-feeding animals. Poisoning of aquatic life will also arise from cadmium.

The discharge of phosphogypsum slurry into holding ponds results in wastewater with high concentrations of phosphate, fluoride, sulphate and calcium ions, and high acidity (pH 1.0-1.5). If this pond water enters natural surface waters it can damage aquatic life.

(iii) Groundwater pollution

There is a possibility that groundwater can be contaminated by slurry pond water leaching downwards to the water table. High concentrations of nitrates in groundwater are a health hazard (especially to babies). High concentrations of fluoride in potable groundwater can lead to tooth damage. Cadmium, arsenic and vanadium contamination of groundwater render it unsuitable for most purposes.

(iv) Soil pollution

The major problem associated with the dumping of phosphogypsum on land is its acidity which prevents plant growth. High concentrations of fluoride in the soil are also likely to affect plant growth.

Figure 5.1 *The Agrochemicals (Fertilisers) Industry*

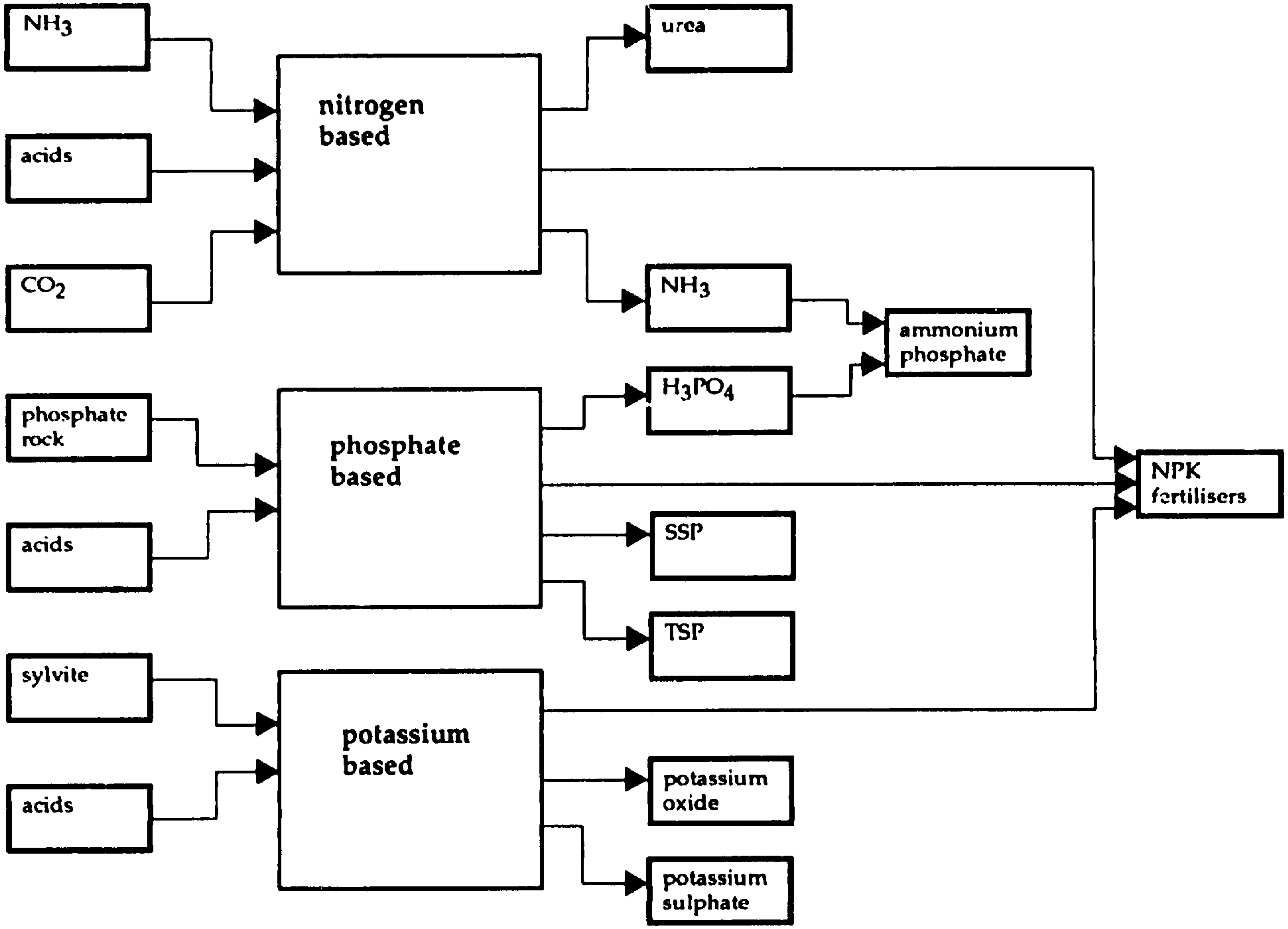
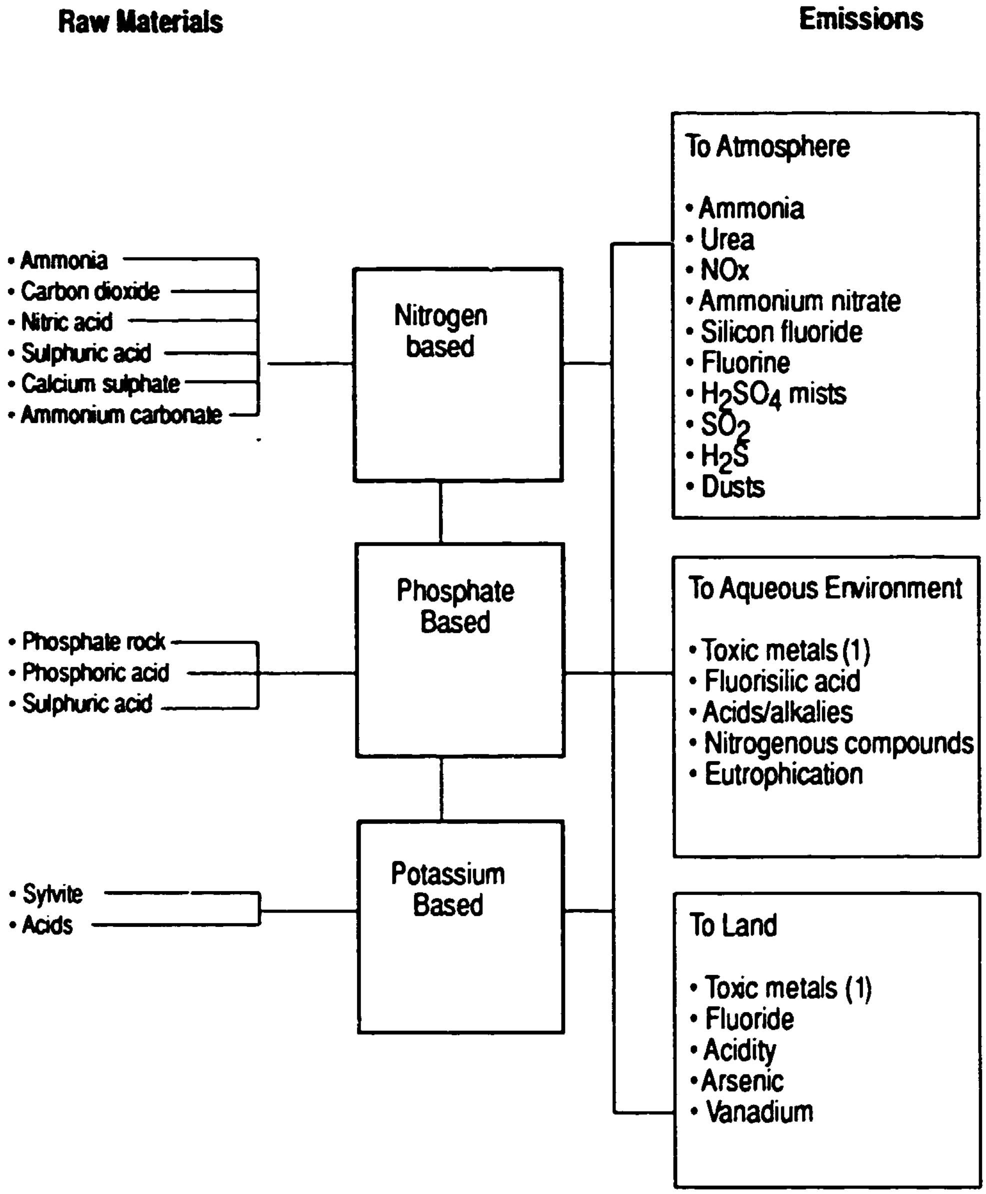


Figure 5.2 ***Raw Materials and Emissions***
The Agrochemicals (Fertilisers) Industry



Note 1: Depending on route of disposal of phosphogypsum

6 POLLUTION FROM THE METAL PREPARATION AND FINISHING INDUSTRY - SOURCES, EMISSIONS AND EFFECTS

6.1 THE INDUSTRY AND THE ENVIRONMENT

The metal preparation and finishing industry involves the following surface improvement processes:

- Surface preparation by cleaning
    - acid or alkaline cleaning
    - bright dipping
    - pickling
    - emulsion cleaning
    - mechanical cleaning
    - salt bath descaling
    - solvent cleaning
    - ultrasonic cleaning
- Hardening (case hardening) or softening (annealing)
- Smoothing (polishing) or roughening (buffing)
- Metal deposition by electrolytic technique (electroplating)
- Surface conversion by chemical deposition (phosphating)
- Surface coating with organic materials (conversion coating)
- Electrocoating of surface with organic materials (electropainting)
- Surface oxidation by electrolysis (anodizing)

The industry can be considered in two principal segments:

- 'captive' establishments designed to handle a known and regular throughput; and
- 'jobbing' establishments which provide a metal preparation and finishing service on demand from external clients.

The industry uses in excess of 100 different chemicals and electroplating solutions.

Wastes generated contain heavy metals, acid, alkalies and solvents, and are considered to be potentially hazardous both in relation to discharges to aqueous environment (direct impact) and to land. The latter is particularly important as metals and solvents can easily become a part of the leachate from landfill operations with potential to drain into surface waters and underground water supplies. The industry also releases significant quantities of solvents, acid fumes and mists to atmosphere.

6.2 *THE INDUSTRY IN CONTEXT*

This section of the paper attempts to relate the scale of metal preparation and finishing industry to the indigenous manufacturing base. For example, the scale of metal finishing is considered on par with production of goods such as bicycles, household goods, automobiles etc.

Countries such as China and India have all experienced rapid growth in the general engineering sectors. For example, the total number of automobile and motor cycle manufacturers in China has grown rapidly in recent years and now exceeds 4000. Bicycle manufacture in 1989 was more than 36.5 million units, and alone supported a buoyant metal finishing sector. In India, production of general engineering items has risen from Rs 34.7 billion in 1970/71 to an estimated Rs 593.7 billion in 1988/89. Following from this, the latest index of production for engineering industries was 177.6 in 1987/88.

The engineering industry in Pakistan encompasses 1900 registered enterprises, employs around 205,000 persons and has an annual production of around Rs 17.5 billion worth of engineering goods. The range of goods now produced includes engines, cars, machinery, household appliances, office machines and radios and has caused a corresponding growth in the metal finishing industry. From UNIDO figures available (Industrial Development Review Series, 1990) local production of metal goods has increased from Rs 992 million in 1981/82 to 2,338 million in 1987/88.

Thailand has a significant metal finishing industry which is primarily geared towards the automobile industry. Specialised processes such as heat treatment tend to be carried out by larger companies in their own factories, although there are some companies such as PKN Co and Mahachak Group who offer the service. Other areas such as pressworking, stamping, and plating tend to performed by smaller companies for electrical appliance manufacturers and the motor vehicle component market.

Indonesia's engineering industry includes manufacture of intermediate products, parts and components, and assembly operations. Although having a reasonably small base, the capital goods and engineering sector is a fast growing branch of the overall Indonesian manufacturing industry. Among the major branches of the engineering sector the largest areas are transport equipment, metal products and electrical machinery, with employment in large and medium scale enterprises reaching 176,950 in 1985

Countries such as Bangladesh and Viet Nam generally face constraints of low technology levels and outdated equipment. Regardless, figures available from The Economist Intelligence Unit (Bangladesh Country Profile 1991/92) indicate that production value of fabricated metal products increased from Tk

1,088 million in 1983/84 to Tk 1,454 million in 1987/88. This expansion is likely to have been replicated in the metal finishing industry. The engineering/metalworking industry also represents an important component of Viet Nam's manufacturing sector as a whole, currently accounting for some 14 percent of total manufacturing value. Some 300,000 people are employed throughout the country, of which about 30,000 are skilled workers.

6.3 *PROCESSING AND PRODUCTION METHODS*

6.3.1 *General*

The industry is depicted diagrammatically on *Figure 6.1*.

The service offered by the industry may vary from a single operation to multiple-step processing. Operations can be divided into three different categories:

- mechanical
- chemical
- electrochemical

Mechanical operations include:

- grinding
- grit or shot blasting
- buffing
- deburring
- polishing

Chemical processes include:

- degreasing
- acid pickling
- alkaline cleaning
- acid cleaning
- surface neutralising
- chromating
- phosphating
- bright dipping
- chemical polishing
- passivation
- stripping

Special cases in this latter category include electroless nickel and electroless copper plating in which the surface of the workpiece acts as a catalyst for the decomposition of the solution with the deposition of the metal on the workpiece.

Electrochemical processes include:

- anodic cleaning
- cathodic cleaning
- anodising
- electroplating

6.3.2 *Preparation Processes*

A typical electroplating process includes cleaning, electroplating, rinsing and drying. The cleaning operation consists of two or more steps that are required for removing grease, oil, soil and oxide films from the base metal surface and ensuring good electroplate adhesion. Sequential treatments in an alkaline solution and then in an acid solution with intermediate rinsing are the minimum generally required for good processing. Typical pretreatment sequences for electroplating and anodizing of aluminium appear on *Figure 6.2.*

6.3.3 *Finishing Processes*

Metal deposition can occur from acid or alkaline solutions. The most important acid plating baths contain the metal salt in the form of sulphate or chloride or a mixture of the two with some free acid present and some inorganic buffer to maintain a specific solution pH. The most important alkaline plating baths contain the metal salt in the form of cyanide.

The metal ions in solution are usually replenished by dissolution of the metal from anodes in bar form or in small pieces contained in inert or expanded metal baskets. Replenishment with metal salts also is practised, particularly for chromium plating. In this case an inert material must be selected for the anodes.

Hundreds of different electroplating solutions have been adopted commercially but only two or three types are utilised widely. Cyanide based solutions are popular for copper, zinc, brass, cadmium, silver and gold. Non cyanide alkaline solutions containing pyrophosphate or other chelating agents have come into use for zinc and copper. Acid sulphate and/or chloride solutions also are used for zinc, copper, tin and nickel, particularly for the plating of relatively simple shapes. Cadmium and zinc are also electroplated from neutral or slightly acid chloride solutions.

Surface treatments include anodising, chemical brightening, electroless plating and chromating or other conversion treatment. Some of these treatments are carried out prior to electroplating, some after electroplating and some instead of electroplating.

Conversion coatings of zinc and iron phosphates are applied to steel as preparation for subsequent organic coatings and for lubricating in forming dyes.

Barrel plating is used for small parts that tumble freely in rotating barrels. Rack plating generally is used for larger parts, the rack being designed to carry current equally to the number of parts being plated.

Mechanical transfer systems are used for barrel systems. Rack systems can be manual or mechanised.

For products such as wire or steel strip, continuous metal preparation and finishing systems are generally used.

6.4 *USE/GENERATION OF CHEMICALS*

Over 100 different chemicals could be used by a typical metal preparation and finishing establishment; the principal chemicals or groups being listed in *Figure* 6.3.

Most chemicals actually used in a metal preparation and finishing establishments appear in the wastes discharged from the process lines (in original or modified form) together with those constituents of the input metal or components which are dissolved or removed during the preparation and finishing processes. Possible exceptions include gold and silver where recovery systems are well established and economically viable within a short time scale.

In *Figure* 6.3 an important group of chemicals are noted under the heading 'complexing/chelating compounds'. These chemicals are often added to proprietary mixes to prevent premature deposition of metals or the components present in the electroplating environment. When present in waste streams such complexing agents can inhibit conventional metal precipitation and removal processes depending on the relative complexing power of the additive.

Typical complexing agents, and their relative complexing powers in relation to cadmium, copper, nickel and zinc are shown in *Table 6.4a* below.

Table 6.4a Relative Complexing Powers of Some Metal Ion Complexing Agents

Complexing agent	Cadmium	Copper	Nickel	Zinc
Ammonia	2.55	4.04	2.72	2.21
Citrate	3.75	5.90	5.40	4.98
Monoethanolamine	2.80	5.70	2.98	3.70
Ethylenediamine	5.41	10.48	7.32	5.66
EDTA	16.36	18.70	18.52	16.44
Oxalate	3.89	6.23	5.16	4.87
Pyrophosphate	-	7.60	5.94	8.70

Source: Chemical Processes in Wastewater Treatment - W J Eilbeck and G Mattock

Constituents of the input metal or components which are dissolved or removed during preparation and finishing processes and which appear in waste emissions include:

- oil and grease in insoluble and emulsified form;
- base metal dissolved during pickling processes;
- general scale and suspended solids;
- metals or elements stripped from components by renovative type processes;
- chemicals used in effluent treatment processes including:
    - sodium hydroxide
    - sodium carbonate
    - calcium hydroxide
    - sulphur dioxide
    - sodium bisulphite/metabisulphite
    - chlorine
    - sodium hypochlorite
    - ferric chloride/sulphate
    - coagulant and flocculant aids
    - specific metal precipitants

Specific metal precipitants (sometimes added to enhance removal of toxic metals prior to discharge) include:

- Tri mercapto triazine trisodium salt
- Di ethyl thio carbamate
- Di methyl thio carbamate

6.5 *EMISSIONS AND EFFECTS*

6.5.1 *Emissions to Aqueous Environment*

Emissions to aqueous environment essentially comprise continuous flow rinse waters which follow each preparation or finishing process plus periodic discharges of strong process solutions when spent or contaminated. There are also emissions from spillages and leakages, aqueous phase discharges from fume scrubbing equipment etc.

Such discharges contain the raw materials used in processing in original or modified form plus constituents dissolved or removed from the components processed. They can be highly acidic or alkaline in nature, contain free and complexed cyanide and potentially contain toxic metals up to a few hundred mg/l in concentration.

Many of the components in emissions from metal preparation and finishing establishments are immediately toxic to equatic organisms and fish life and corrosive to plant and equipment. Direct discharges from such establishments must be avoided.

To minimise impact on the aqueous environment treatment is carried out to neutralise acids and alkalies present in the discharge and to precipitate and remove toxic metals. Typically this is achieved by pH adjustment using sodium or calcium hydroxide to neutralise acidity and to generate relatively insoluble metal hydroxides (hydrous metal oxides), as depicted by the following reactions in *Table 6.5a*.

Table 6.5a ***Neutralisation Reactions***

Neutralisation Reactions						
H_2SO_4 Sulphuric acid	+	NaOH Sodium hydroxide	—>	Na_2SO_4 Sodium sulphate	+	$2H_2O$
HCl Hydrochloric acid	+	$Ca(OH)_2$ Calcium hydroxide	—>	$CaCl_2$ Calcium chloride	+	$2H_2O$
Precipitation reactions						
$NiSO_4$ Nickel sulphate	+	$Ca(OH)_2$ Calcium hydroxide	—>	$CaCl_2$ Calcium chloride	+	$2H_2O$
$CuSO_4$ Copper sulphate+	+	2NaOH	—>	$Cu(OH)_2$	+	Na_2SO_4
$FeSO_4$ Ferrous sulphate	+	$Ca(OH)_2$	—>	$Fe(OH)_2$ Ferrous hydroxide	+	$CaSO_4$
$Fe(SO_4)_3$ Ferric sulphate	+	$3Ca(OH)_2$	—>	$2Fe(OH)_3$ Ferric hydroxide	+	$3CaSO_4$

Essential pretreatments prior to metal precipitation include:

- reduction of hexavelant chromium to its trivalent form using a sulphur dioxide containing reductant;
- oxidation of cyanide to cyanate to destroy cyanide-metal complexes; also to reduce potential toxicity.

A schematic of a typical process water flow and wastewater treatment scheme appears as *Figure 6.4*. A diagram of a typical continuous wastewater treatment plant based on the principles described appears as *Figure 6.5*.

Such reactions are generally sufficient to reduce the concentration of metals in a mixed metal preparation and finishing wastewater to less than 1 to 2 mg/l on an individual basis, ie between 5 and 10 mg/l in total; also to reduce free cyanide to less than 1 mg/l. However in many instances this is insufficient to meet environmental objectives.

Potential difficulties experienced by the industry in achieving low residual metals include:

- the problem of a requirement for differing optimum precipitation control points on a metal by metal basis (*Figure 6.6* shows residual soluble metal concentrations using sodium hydroxide and calcium hydroxide reagent);

- inefficient solids capture (by sedimentation, flotation or filtration) after precipitation;

- presence of complexing agents.

Potential solutions to achievement of low metal residuals include:

- enhanced removal of residual precipitants through:

  - optimisation of conditions for coagulation and flocculation including co-precipitation;
  - provision of media filtration;
  - provision of microfiltration;

- enhanced removal of residual soluble metals through use of:

  - chelating ion exchange resins
  - adsorbents
  - specific precipitant chemicals such as tri mercapto triazine trisodium salt, diethyl thio carbonate or dimethyl thio carbonate;

- shift of emphasis from 'end of pipe' to 'integrated source control'.

The major problem associated with achievement of low metal residuals concerns the presence of strong metal complexes which do not respond to most of the procedures noted above. *Figure 6.7* depicts the extent of additional treatment that can sometimes be required to accommodate strong metal complexes. Under such circumstances a switch in emphasis from 'end of pipe' to 'integrated source control' is the preferred solution.

6.5.2 *Emissions to Land*

Potential emissions to land from metal preparation and finishing establishments include:

- spent process solutions after individual treatment at the point of origin or at the point of disposal to effect neutralisation of acids/alkalies and conversion of soluble toxic metals into an insoluble form;

- grinding materials from mechanical cleaning operations;

- dewatered metal hydroxide containing sludges from the wastewater treatment facility;

- general process sludges and deposits including plant clean outs;

- spent filter cartridges (carbon and membrane) from in-line cleaning duties.

Potential problems include release of metals to surface water or ground water in the event that deposit sites become contaminated with liquors acidic in nature. In addition, there is potential crop metal uptake.

6.5.3 *Emissions to Atmosphere*

Emissions to atmosphere from metal preparation and finishing establishments include:

- volatile organic compounds from open metal cleaning and degreasing units based on the use of solvents such as trichloroethylene, trichloromethane, trichloro trifluoroethylene, methylene chloride etc.

- acid mists and fumes arising from process vats including those maintained at elevated temperatures.

Generally, points of emission (individually or in combination) are provided with containment and control facilities based on wet scrubbing which in turn leads to discharge to the aqueous environment.

Strict in-plant segregation of acid and cyanide based liquors must be maintained, to prevent the risk of production of extremely toxic hydrogen cyanide gas.

Additional strict in-plant segregation of acid and sulphide based liquors must be maintained to prevent release to atmosphere of toxic hydrogen sulphide gas.

Figure 6.1 *The Metal Preparation and Finishing Industry*

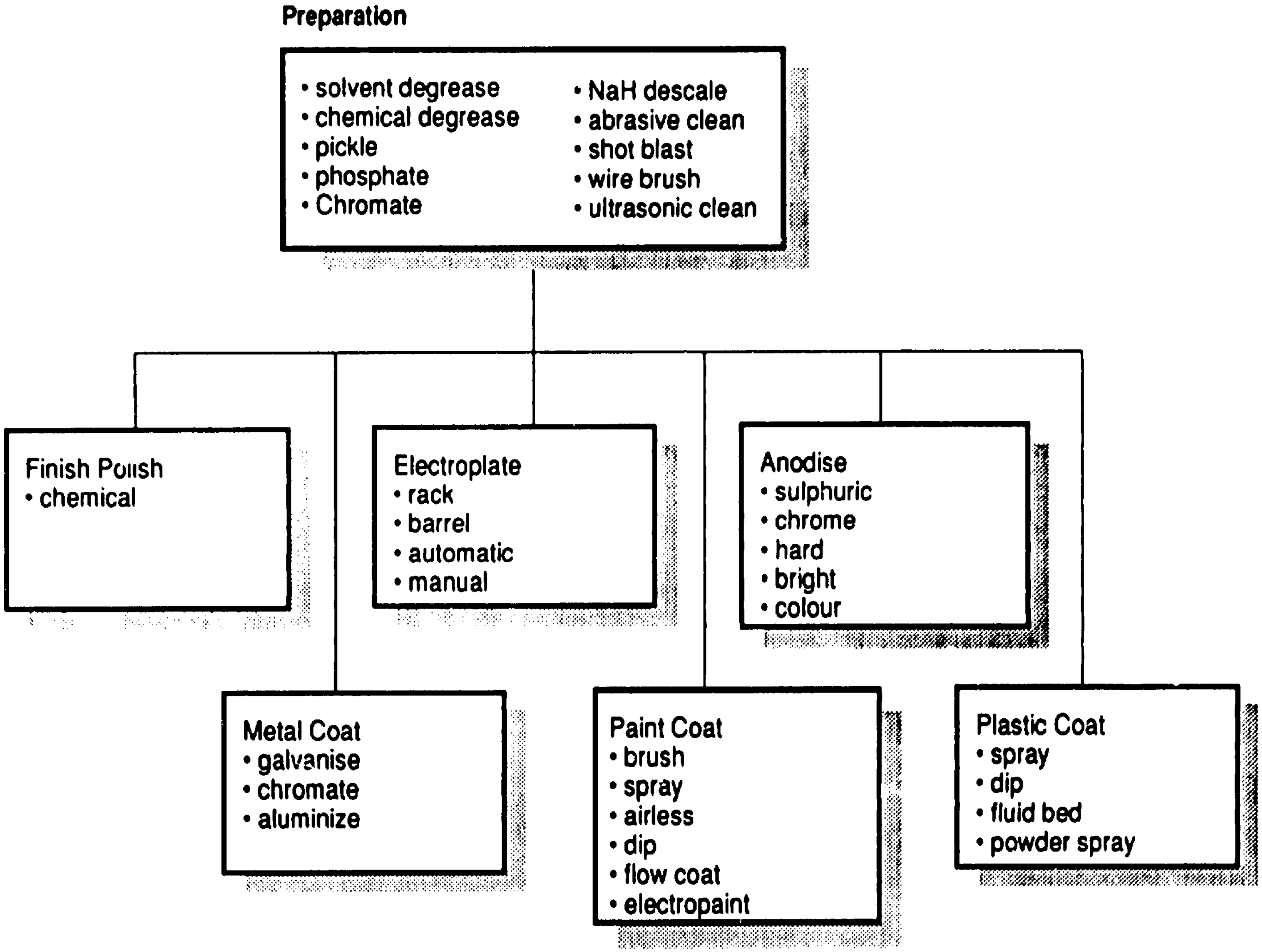
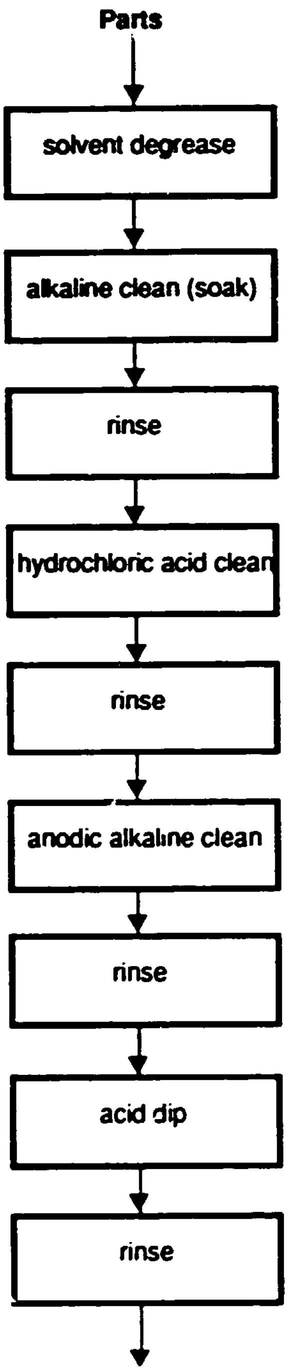
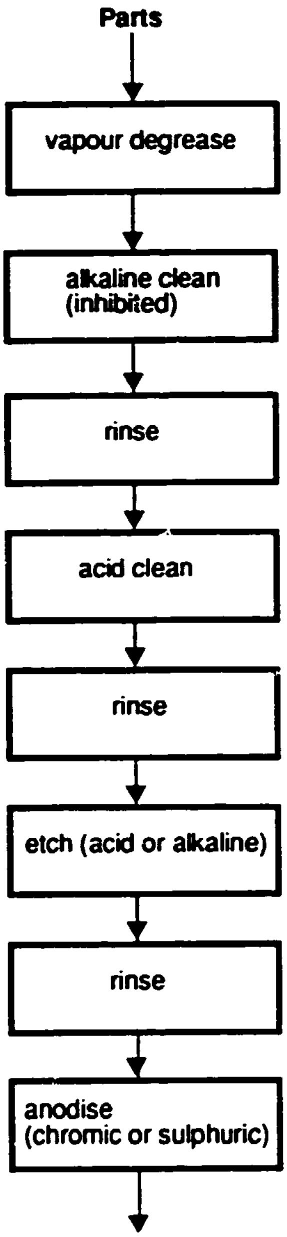


Figure 6.2 ***Typical Pretreatment Sequences***

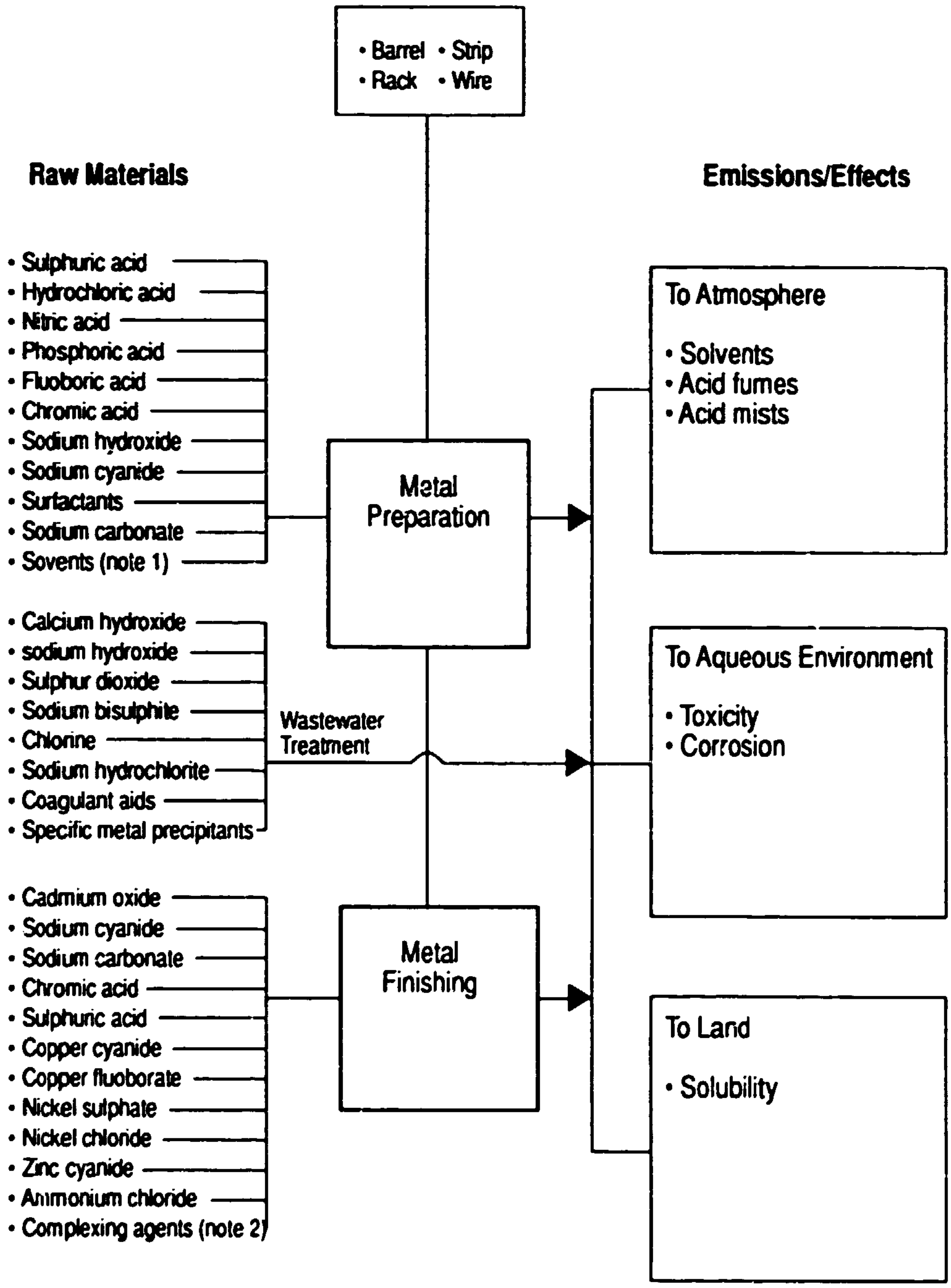


Typical Pretreatment Sequence
- Electroplating



Typical Pretreatment Sequence
- Anodising of Aluminium

Figure 6.3 *Raw Materials and Emissions*
The Metal Preparation and Finishing Industry



Note 1: Trichloroethylene, trichloroethane, trichlorotrifluoroethylene, methylene chloride

Note 2: Ammonia, citric acid, monoethanolamine, ethylenediamine, EDTA, oxalate, pyrophosphate

Figure 6.4 ***The Metal Preparation and Finishing Industry***

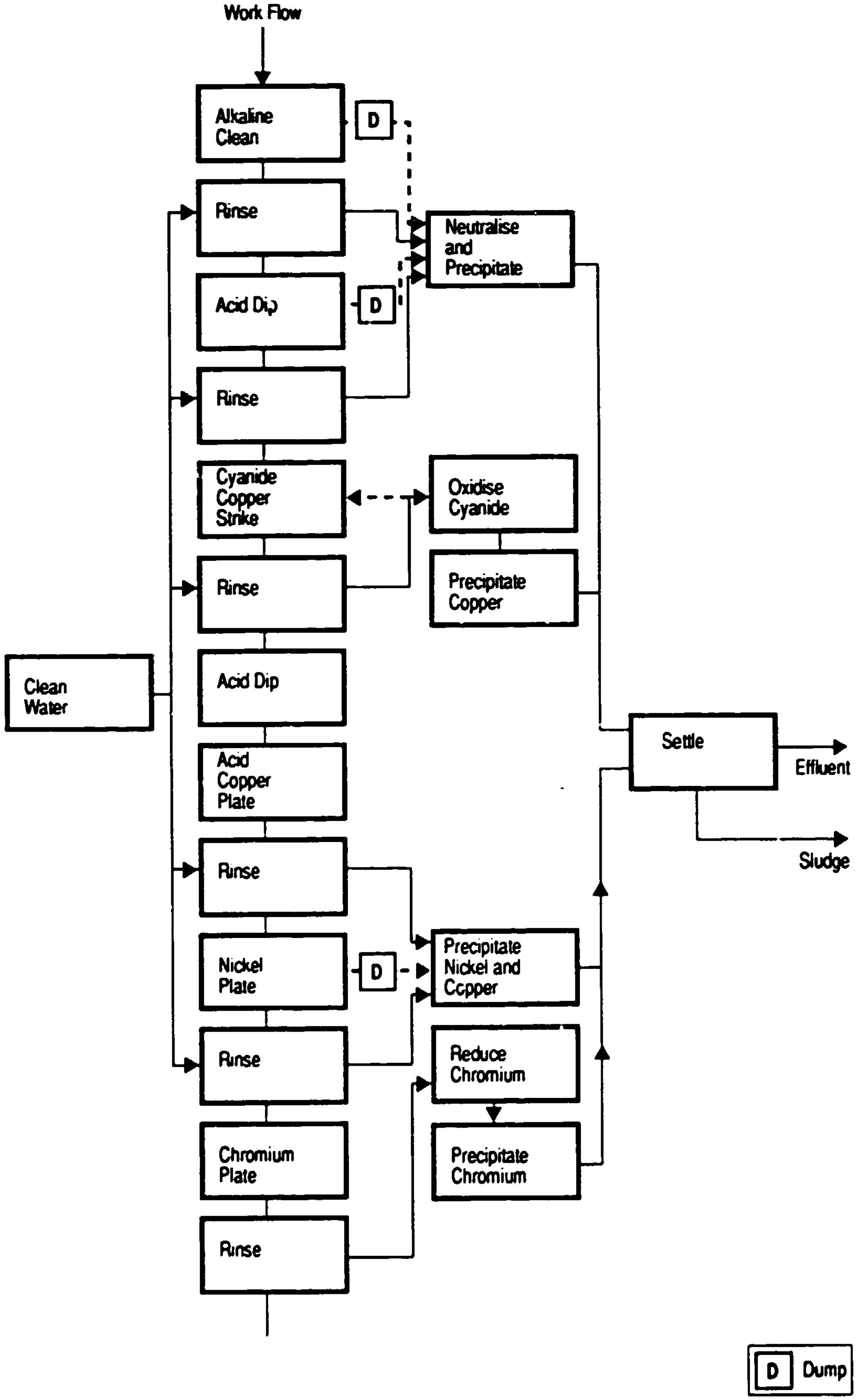


Figure 6.5 *The Metal Fininshing Industry*
Diagram of Typical Continuous Treatment Plant

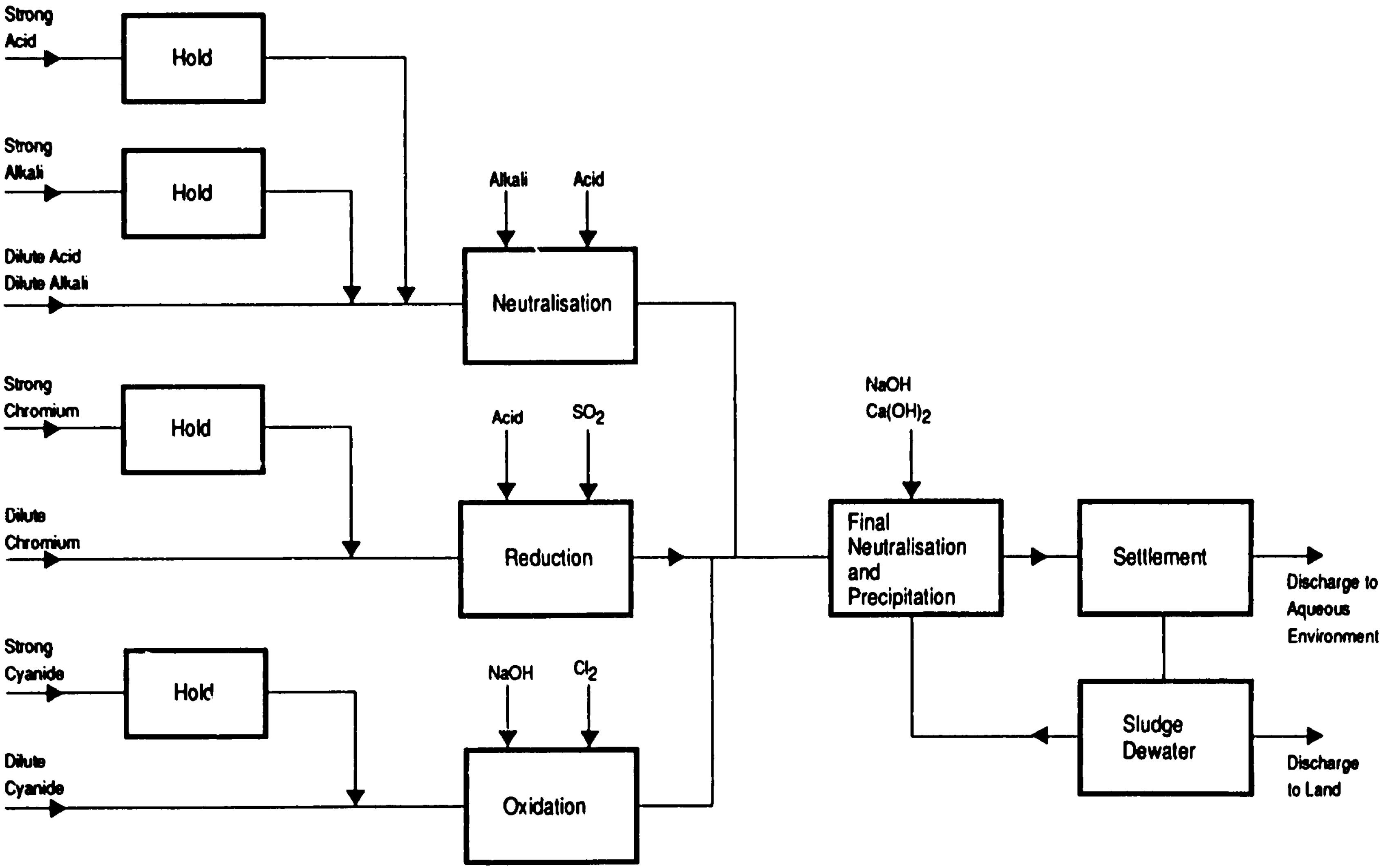


Figure 6.6 *Toxic Metal Precipitation*

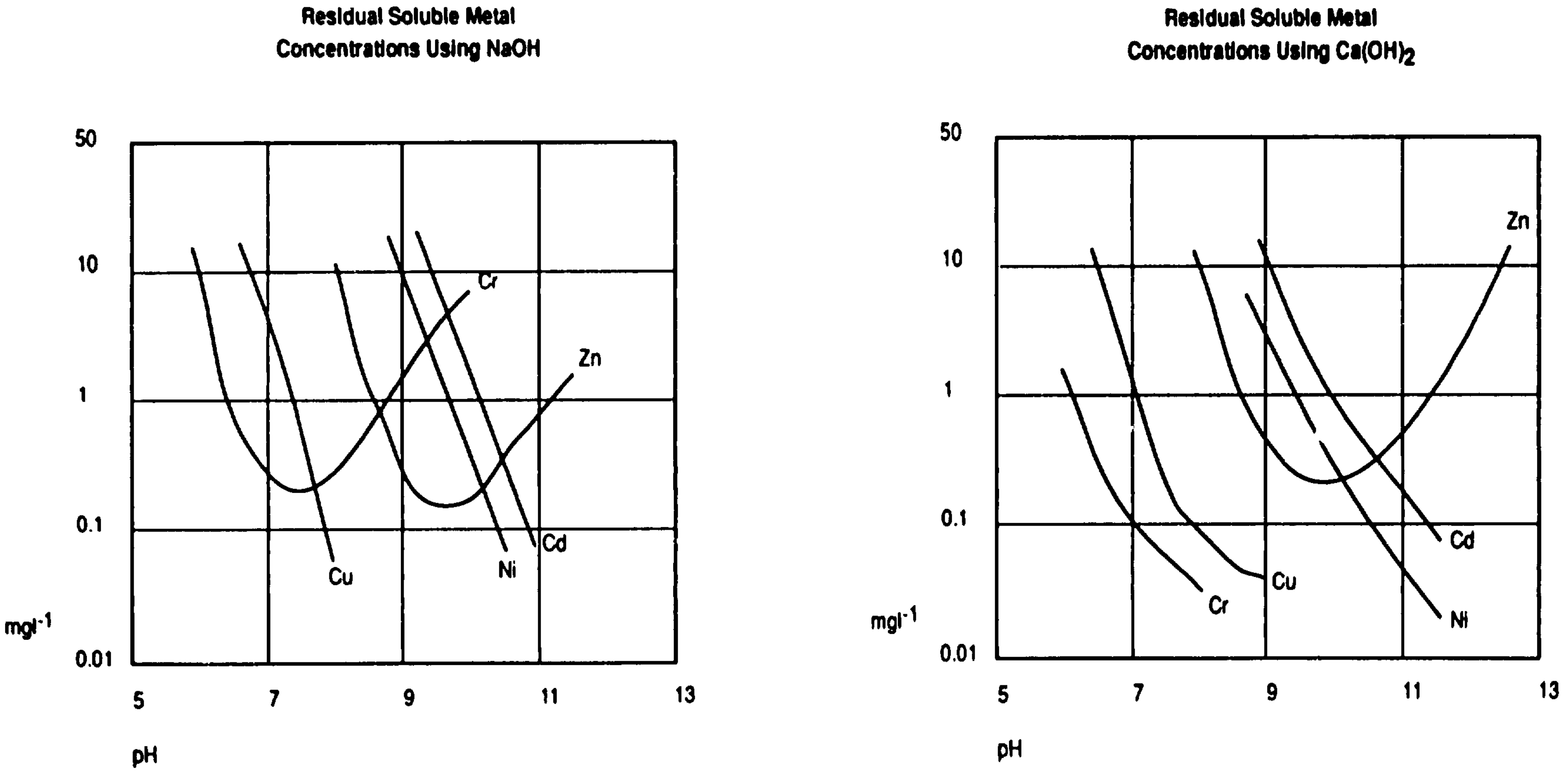
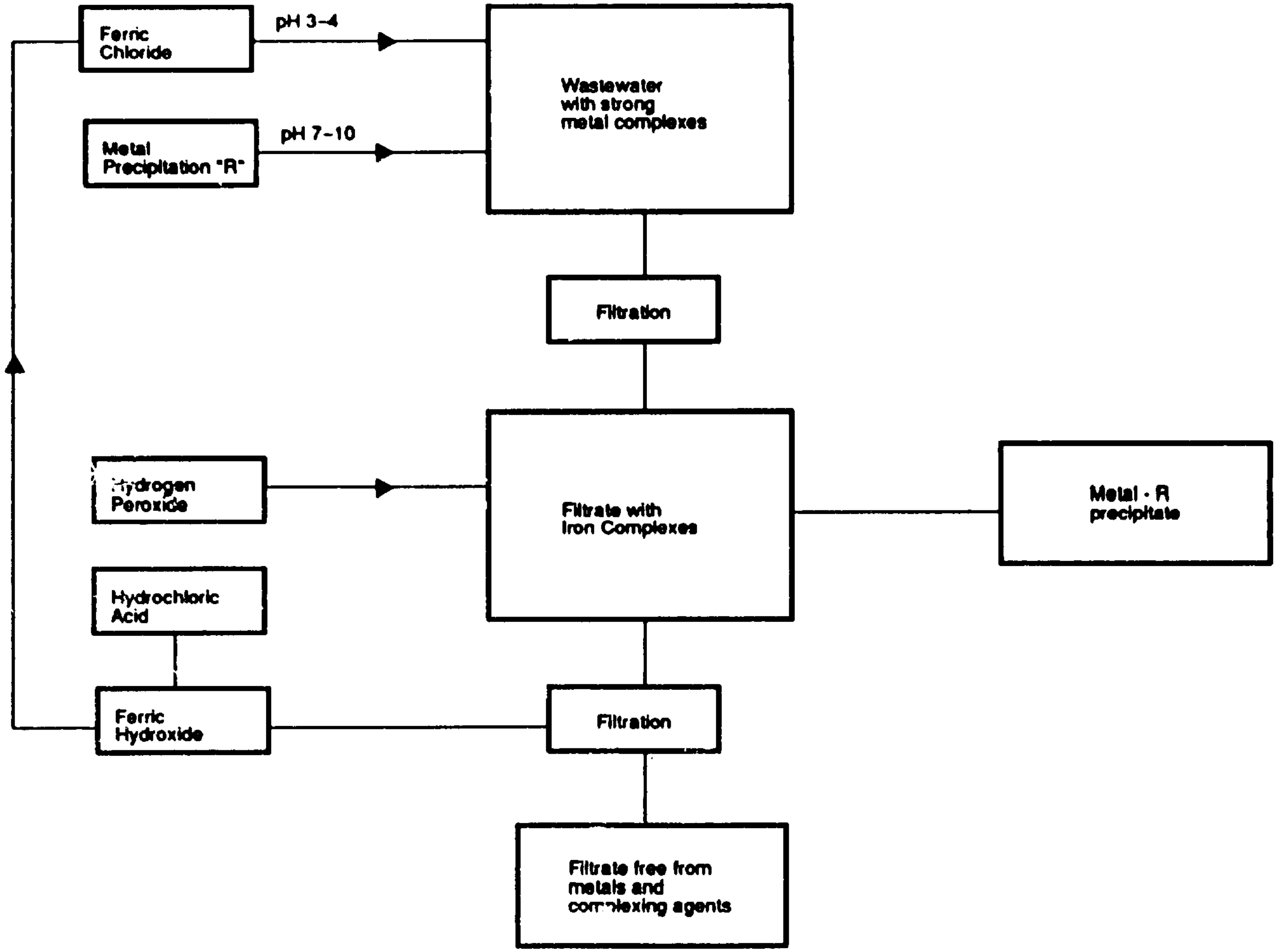


Figure 6.7 *Metal Precipitation in the Presence of Strong Complexing Agents*



7 *POLLUTION FROM THE ELECTRONICS INDUSTRY - SOURCES, EMISSIONS AND EFFECTS*

7.1 *THE INDUSTRY AND THE ENVIRONMENT*

The 'electronics' industry covers a wide range of activities which embrace production of integrated circuits as well as numerous metal preparation and finishing processes. This chapter reviews the industry with emphasis on production of integrated circuits only; the metal preparation and finishing industry having been covered in Chapter 6.

The semiconductor industry has grown at a high rate over the last twenty years. Today semiconductor devices (integrated circuits) are used in areas such as consumer products, computers and the defence industry, and impacts on almost all areas of life.

Semiconductor manufacturing is the art of miniaturisation and, although integrated circuits are manufactured in billions of devices every year, the manufacturing processes themselves operate on a small scale.

Production of integrated circuits is carried out in clean room areas and in almost laboratory style batch systems. Silicon wafers - typically 150mm diameter - are the starting point and are produced by specialist suppliers. These are processed in batches of about ten at a time in a series of processing stations, rinse batches and furnaces.

The chemicals used in manufacturing are highly toxic and hazardous. However, they are used in relatively small quantities and are tightly controlled. The largest consumption is that of ultrapure water, which is used in copious quantities for rinsing at almost every stage of manufacture. It is the production of this water which probably creates the largest waste stream in most semiconductor plants.

Other potential impacts on the environment include discharge of spent acids, non regenerable ion exchange resins, used filter cartridges and various emissions to atmosphere.

7.2 *THE INDUSTRY IN CONTEXT*

7.2.1 *Bangladesh*

The electronics industry in Bangladesh occupies only a small part of overall industrial production. In recent years, the movement into electronics has shown an increasing trend, with a number of foreign investors setting up light electronics assembly plants in the Chittagong export processing zone (EPZ). This movement is partly to escape rising wages in other Asian countries, and as a result, a second EPZ at Chittagong is to be built which should consolidate this trend.

7.2.2 *China*

China is a relatively small electronics producer by international standards, accounting for about 0.2% of global production. The industry is primarily orientated to the huge domestic market, and is among the fastest growing segments of the engineering branches.

Roughly 50% of the gross output value of the electronics industry is categorised under light industry production. Geographically, the industry is mainly concentrated in the coastal provinces. Beijing, Tianyian, Shanghai, Jiangsu and Guangdong accounted for approximately 60% of gross industrial value in the late 1980's with the only non-coastal province having a sizeable electronics industry being Sichuan.

The electronics industry tends to be concentrated and has a number of large companies. For example, eight firms with assets in excess of Rmb 300 million account for roughly a fifth of gross output value. The overall performance of the industry in terms of the growth in output of many products is impressive. From 1978 to 1987, the average annual growth rate of the electronics industry exceeded 20%. During 1988, a 30% increase in gross output was achieved.

The most successful product launched by the electronics industry in recent years has been colour television, although the computer and electrical appliances industries have witnessed rapid development. Specifically with regard to computers, a growing emphasis has been placed on the production and use of micro-and mini-computers, and they have subsequently found wide application in the petroleum, chemical, metallurgical, power, textiles, shipbuildings, astronautics and nuclear industries.

Overall, future growth in the electronics industry will continue to be fuelled by a significant increase in domestic demand. Although in the late 1980's there were 1000 enterprises turning out a gross output value of Rmb 24 billion, China is taking on the challenge to increase electronics production and to become more competitive in the international area. This challenge is gradually being achieved by foreign investment in the form of technology import and joint ventures.

7.2.3 *India*

In 1989, India had approximately 2600 electronic/electrical companies employing about 230000 people. Output of electronic equipment and components reached US$ 4039 million, of which exports represented only 2%. The contribution of the industry to India's GNP almost doubled from 1985 to 1990 (now standing at 25% of GNP), with consumer electronics being the driving force. Other main production activities include components, telecommunications equipment, control and instrumentation.

India's consumer electronics industry has come to dominate the electronics sector. It accounts for at least 500 companies of which more than 80% are small-scale manufacturers assembling kits. However, the Planning commission is keen to end 'kit culture' and strengthen the indigenous base of the electronics industry. Television manufacturing has led to big growth in the consumer electronics industry and now accounts for over 70% of the sector's output. Additional consumer products recently introduced include electronic watches and clocks, and alternative sectors of considerable growth include the manufacture of computer hardware, and of components.

The industry is strongly supported by the government, with the public sector playing a dominant role in production. Emphasis is being placed on the integrated development of the electronics industries in the next decade, with a view to reducing the dependence on imports. The export processing zones in different parts of India have been attracting enterprises from developed countries to produce cheaper components and equipment. This is in an effort to export products from these zones to areas advantageously located or even to the developed countries.

7.2.4 *Indonesia*

The Indonesian electronics industry is dominated by the consumer and component sectors. There are over 200 electronics/electrical companies employing approximately 25000 people, with the major companies including Inti, Panatraco, Philips Ralin Electronics and Sanyo Industries Indonesia. A large proportion of the industry is located in Java, although some can be found in northern Sumatra.

An Electronics Commission was set up in 1984, and since the establishment of this Commission the government has made considerable effort to develop the electronics industry. Moves have included a package of new incentives to attract foreign investors in the form of joint ventures and export promotions (May 1986), and the intention to ban imports of microcomputers and other electronic goods. High priority has been given to the expansion of Indonesia's telecommunications system, and it is likely that private investors will be invited to have some involvement in the development and operation of public telephone networks.

Indonesia's output of electronic equipment and components was valued at US$ 1.0 billion in 1988, with exports representing nearly 17% of this figure. However, there was a substantial trade deficit in this sector (US$ 406 million) arising from imports of US$ 575 million.

7.2.5 *The Republic of Korea*

Korea is one of the world's largest electronics manufacturers. The industry is similar in size to the UK and France, and is exceeded only by the US, Japan and Germany. Broadly speaking, the industry can be categorised into three sub-sectors of consumer electronics, parts and components, and industrial electronics, with leading products being PC monitors, telephone systems, cellular telephones, semiconductors, microwave ovens and televisions.

Although in 1988 there were 1251 electronics companies employing 410,000 people, the industry is dominated by just three companies; Goldstar, Samsung Electronics and Dalwoo Electronics. These three companies account for 57% of the industry's sales.

In 1989, electronics finally overtook textiles to become Korea's largest export earner. Production value of electronic equipment and components reached US$ 22.5 billion, with exports representing US$15.1 billion, or around 67%. This production accounted for a quarter of total South Korean exports (The Economist Intelligence Unit Special Report No. 2005, 1989). Electronics has been given the term 'a strategic industry' by the government, with the Ministry of Communication (MOC) recently announcing a plan to foster Korea's information and telecommunications industry. As a result, there have been designated 18 priority technologies in semiconductors, telecommunications and computers, and the MOC has indicated it will set up leasing companies to support R&D efforts.

In general, major Korean electronic appliance makers are expanding their overseas production facilities and relocating highly labour intensive functions to cheaper Asian countries and Mexico. This has been in direct response to the following factors:

- the need to secure market access in protectionist western countries, particularly the EC;
- the strong Korean won weakening international competitiveness;
- rising local wages and labour unrest.

As a result of these factors, growth of electronics production is forecast at only 5% for 1991, down from 7% in 1990 and 20% in 1989 (Elsevier World Electronics Companies File 1990/91).

7.2.6 *Malaysia*

Malaysia's electronics industry was established in the early 1970's and has been a driving force behind the country's change-over from a commodity producer to a manufacturing power. From four electronics companies producing consumer products in 1970, the industry has grown to 187 companies (1988) producing components and consumer and industrial electronics. The electronics industry was the biggest export earner in 1988, accounting for 56% of all manufactured exports at a value of US$ 5.5 billion.

Activities in the manufacture of electronic components mainly involve the assembly and test activities of semiconductors (more than 80 percent) and other electronic devices from basic imported units such as wafers or chips. Consumer electronics, which account for approximately 10-15% of output, is mainly concentrated in the assembly of home entertainment products and electronic household goods. The relatively small industrial and commercial electronic subsector primarily manufactures equipment such as telecommunication equipment, telephone switching, radio phones, junction boxes and mobile radios.

In recent years the electronics industry has been undergoing major structural changes with increasing foreign investment. There has been a significant influx of small and medium-sized firms from Taiwan and Hong Kong. These companies are increasing diversity in an industry previously dominated by the big names in the US, European and Japanese electronics industry.

Although there is a general shortage of experienced engineers, the labour force is becoming increasingly skilled. This, is conjunction with a good infrastructure and an attractive investment climate, means the electronics industry is expected to undertake a significant amount of its own product design in the 1990's.

A major constraint has been the absence of a big end-user's market in Malaysia, unlike in Taiwan Province and the Republic of Korea. This lack of domestic market is unfavourable to small-sized and Malaysian-owned companies. For example, in the free-trade zones outside Kuala Lumpur and Penang, Malaysia's component industry now includes nine of the world's ten largest suppliers of semiconductors.

Finally, a key issue is the management of the growth of the industry. To date, there have been inadequate provisions foreseen for the disposal of neutralised waste generated, and signs of strain on the infrastructural facilities are starting to emerge. These problems will need to be addressed in order to keep pace with demand for new facilities.

7.2.7 *Pakistan*

Although all categories of engineering products in Pakistan have shown an upward trend, in 1987/88 there was a striking increase of output by the electronics and transport equipment industries. Results by UNIDO (1990) indicate that the value of local production of electronics goods has increased from Rs 785 million in 1981/82 to Rs 2380 million in 1987/88.

7.2.8 *The Philippines*

The Philippine electronic industry is a significant contributor to exports, with the most important segment of the industry being the semiconductor branch, (which accounted for about 96% of electronics imports in 1986). Other activities comprise assembly activities and consumer electronics.

The core of the semiconductor branch in the Philippines is the labour-intensive part of integrated circuits production. Major companies in the semiconductor industry are either third party subcontractors which are mainly Filipino owned, or subsidiaries of multinationals such as Advanced Micro Devices, General Electric, 3M, Motorola, Intel, Texas Instruments, Data General, Schlumberger, Gould and IBM.

There are currently 28 operating semiconductor firms in the Philippines, with ten being multinationals and accounting for about 73% of total semiconductor exports. The semiconductor industry alone employed 22348 people in 1988, and production in terms of export sales grew by 347% between the years 1982 and 1987.

With regard to computers, the industry is mostly made up of foreign-owned subsidiaries, local distributors, dealers, importers and traders of computer hardware and peripherals. Employment in areas not involved in semiconductors was approximately 27000 people.

Advantages of the Philippines over competing Asian supplier countries lie in cheap labour costs, unfailing delivery, availability of skilled engineers and technicians, well-established multinationals with an intimate knowledge of supply conditions in the Philippines, and minimisation of price undercutting and personnel piracy as a result of growing co-operation among subsidiaries and subcontractors. Weaknesses exist however, in the relatively high power and communication costs, lack of ancillary industries, and in import regulations.

Overall, growth rates of demand for semiconductors are hypothesized to be about 15% with main threats coming from technological innovation and automation. Success in developing a local production centre of electronic equipment beyond semiconductors will depend on liberalised access to imported electronic components and on the simplification of customs clearance procedures.

7.2.9 *Sri Lanka*

Industrial production in Sri Lanka has shown impressive growth rates in the last decade, with most of this development almost exclusively explained by textiles and garments exports. UNIDO statistics indicate that television and radio set exports accounted for US$ 17700, with domestic electrical equipment accounting for US$ 56700. This is insignificant in comparison to main export areas such as textiles, clothing and rubber.

In general, future economic development is facing a number of emerging constraints and perils. In particular, public budget deficits have increased to the point where investment cutbacks seem unavoidable, foreign investment in the Investment Promotion Zone appears to be levelling off, and there is the persistent threat of increasingly violent ethnic conflicts.

7.2.10 *Thailand*

Thailand's electronics industry is undergoing a period of rapid expansion. Due to strong Thai government support, foreign investment is soaring, and the country is becoming a prime destination for Japanese, Korean and Taiwanese electronics manufacturers looking to escape inflated home currencies. It is estimated that there are about 300 electrical and electronic companies in operation, in addition to a large number of supporting industries. Since 1962, Thailand's Board of Investment (BOI) has approved over 249 electronics manufacturing projects in Thailand. By the end of 1988, the industry employed about 131000 workers, and had an output of US$1735 million of which exports represented almost 80%.

There are currently around 15 major electronics companies accounting for a total investment of nearly US$600 million. Although growth in the sector is continuing, there are some weaknesses:

- The relatively small size of domestic and export markets is curtailing optimum growth.
- Excessive red tape to a tax bias against locally - produced equipment and a lack of technology transfer.
- Companies under foreign control dominate 70% of the industry's assets, particularly those with Japanese parents.
- The industrial infrastructure is suffering under the weight of rapid expansion, in particular the telephone network.

In general, although there are shortages of skilled labour, electrical power and water, manufacturers are taking the initiative and providing their own infrastructure. This is expected to aid future growth in the electronics sector.

7.2.11 *Viet Nam*

The general engineering industry manufacturing a wide range of products from electric motors to tools and transport equipment, is an important component of the manufacturing sector as a whole, and currently accounts form some 14% of total manufacturing value in Viet Nam. It is likely that production of electronics in negligible in comparison to the production of engineering equipment.

The engineering industry essentially consists of small and medium-scale enterprises. The principal constraint facing the industry is the generally low level of technology and outdated equipment on which it must rely. In addition to this overriding problem of outdated and poorly maintained machinery, there are a number of other weaknesses which include:

- lack of efficient organisation of production units with respect to plant lay-out, materials flow and work organisation;
- old and outdated consumer goods which make little use of modern electronic parts and components, and therefore generally cannot compete with foreign products on the basis of cost or quality;
- lack of a comprehensive and uniform set of engineering standards.

An increasing consensus is beginning to emerge about the urgent need to overcome these constraints. The rehabilitation and expansion of the engineering industry is expected to be given high priority in future years in an effort to create more employment opportunities, to provide entrepreneurial opportunities for relatively small-scale ventures, and to stimulate growth in other sectors of the economy. This will lead to a need to develop and expand the electronics industry.

7.3 *PRODUCTION AND PROCESSING METHODS*

7.3.1 *General*

Semiconductor production involves a complex and intricate series of operations. The principal stages of the manufacturing process are identified in *Figure 7.1* and summarised briefly below under the headings:

- Acid Etch and Epitaxy Formation.
- Doping and Oxidation.
- Photolithography and Etching.
- Ion Implantation.
- Chemical Vapour Deposition.
- Metallisation.

7.3.2 *Acid Etch and Epitaxy Formation*

The initial process involves growth of additional single-crystal semiconductor material onto a single stage crystal silicon (Si) wafer and essentially comprises:

- acid etching of the wafer using hydrofluoric acid followed by purging at high temperature in a hydrogen atmosphere;

- deposition of Si onto the wafer surface from SiH_2Cl_2 (dichlorosilane) which decomposes to Si and hydrogen chloride gas;

- high temperature treatment to rearrange Si atoms.

7.3.3 *Doping and Oxidation*

Doping involves addition of impurities (dopants) to the Si wafer to give the conductivity properties required. Generally dopants are deposited from special gases, the degree of migration into the Si wafer being dependent on the element deposited. Arsine (AsH_3), diborane (B_2H_6) and phosphine (PH_3) are typical dopants used.

Oxidation involves generation of a layer of oxide on the surface of the Si wafer. This is carried out at high temperature in a controlled oxygen environment.

7.3.4 *Photolithography and Etching*

Photolithography involves establishing predesigned patterns on the silicon wafer through:

- application of a photoresist compound;
- establishment of pattern to be formed using pattern masks or equivalent;
- exposure to UV light to change exposed resist polymer to monomer or vice versa, depending on choice of photoresist (positive or negative);
- removal of underdeveloped photoresist using solvents (trichloroethane, chlorobenzene etc);
- hard 'baking' to assure good photoresist adhesion.

A wide variety of etching acids or gases are used to remove oxide film from those areas of wafer surface not covered by photoresist. Typically hydrofluoric, sulphuric and nitric acids and hydrogen peroxide are used; also gases such as hydrogen chloride or hydrogen fluoride depending on the type of resist.

Organic solvents are then used to remove all remaining photoresist from the wafer.

7.3.5 *Ion Implantation*

This introduces further dopants into the Si structure, typically BF_3 but sometimes 3d and 4d transition elements. Energy, which is controlled by voltage, determines the ion implantation depth. Ions are counted as implantation takes place to regulate the exact amount embedded into the wafer.

7.3.6 *Chemical Vapour Deposition (CVD)*

This process creates various insulating layers on the wafer surface by controlled deposition of atoms following thermal splitting from arsine and/or phosphine.

7.3.7 *Metallisation*

Metallisation involves condensing metal atoms such as silver, nickel and chromium onto the surface of the Si wafer through bombarding pure metal targets with 'ions' under high vacuum.

7.4 USE/GENERATION OF CHEMICALS

7.4.1 *Processing Chemicals*

Chemicals used in the semiconductor manufacturing industry are listed in *Figure* 7.2. Processing chemicals include high purity gases; oxygen, nitrogen, helium, argon, silanes (SiH_4, SiH_2Cl_2 etc) and hydrides (PH_3, NH_3, AsH_3, B_2H_6).

High purity acids are also used depending on the type of semiconductor to be produced (HF, H_2SO_4, HCr, NHO_3).

Photoresists are organic partial polymers which are applied to the silicon wafer. After 'masking' selective etching can take place. The specific chemicals used for etching and the solvents used for removing undeveloped and developed photoresist are generally classified as 'company confidential' but include trichloroethane and chlorobenzene. All chemicals used are high purity (ie better than analytical grade), but quantities are small.

7.4.2 *Utilities*

The principal utility requirement is ultrapure water and this is usually derived from towns mains water. A typical modern semiconductor factory will use about $100m^3/h$ of ultrapure water for washing.

Production of ultrapure water usually involves coagulation with ferric salts (ferric chloride or ferric sulphate), filtration, softening, reverse osmosis, ion exchange and ultrafiltration.

Ultrapure water systems are routinely sanitised using hydrogen peroxide and storage tanks are nitrogen blanketed using high purity nitrogen.

All chemicals and gases including water and air supplies to clean rooms are filtered to less than 0.2 microns using disposal membrane filters.

7.5 EMISSIONS AND EFFECTS

7.5.1 *Emission to Aqueous Environment*

The principal aqueous waste streams are:

- Contaminated waters, mainly from use of high purity water for rinsing duties.
- Etching solutions.
- Solvents.
- Water treatment plant waste.

- Air emission scrubbing systems aqueous phase.

Rinse waters contaminated with trace chemicals are usually so dilute that they can be discharged to sewer untreated. In fact such streams are usually of much higher purity than the raw water supply but may contain organic contaminants which are difficult to remove.

For this reason rinse waters are usually discharged rather than attempting to recover them on the principle that a slight contamination of the ultrapure water system could involve a factory shut down.

The mineral acids used for etching are normally neutralised with lime to precipitate fluoride and toxic metals with sludge being dewatered by filter press or equivalent and neutralised liquor being discharged to sewer.

Discharge direct to water course may require additional controls for removal of trace metals; also enhanced removal of fluoride which remains soluble to about 10mg/l when precipitated as calcium fluoride.

Waste solvents are normally collected and held in drums for disposal off site.

Waste regenerants from production of ultrapure water, generally are neutralised along with etching acids. *Figure* 7.3 depicts typical waste arisings from an ultrapure water facility designed to produce 100m^3/h of ultrapure water.

Disinfectant hydrogen peroxide also is usually discharged via the neutralised plant as are wastewaters arising from air emission scrubbing systems.

Discharges to the aqueous environment from the semiconductor industry are generally of low impact, particularly if conventional end of pipe treatment systems as noted above are applied.

7.5.2 *Emissions to Land*

Potential emissions to land include:

- chemical sludges from the water and wastewater treatment plant; these are generally dewatered to 20 to 25 percent solids content and contain calcium fluoride, calcium sulphate, metal hydroxides and excess calcium hydroxide;
- ion exchange resins (polishing resins are not regenerated);
- spent filter elements (typically PTFE, polypropylene etc);
- spent activated carbon from solvent vent filters etc;
- clean room garments which are increasingly of the disposable type;

- spent solvents and solvent sludges although such waste would generally be disposed of to specialist contractor for recovery or incineration disposal.

Emissions to land are of concern particularly in relation to solvents, which can give rise to significant contamination of groundwater resources on a long term basis.

Other potential concerns include spent activated carbon from solvent vent filters etc.

7.5.3 *Emissions to Atmosphere*

Potential air emissions include all the gas phase chemicals used in production including inert gases, hydrogen , arsine, phosphine and solvent vapours.

Gas emissions are normally vented through appropriate scrubbing systems to atmosphere. The quantities of gases which escape via the venting system are usually very small provided scrubbing systems are installed.

Emissions to atmosphere from semiconductor establishments can be controlled although potential risks include solvent emissions from open vessels etc.

Figure 7.1 *Semiconductor Manufacture*

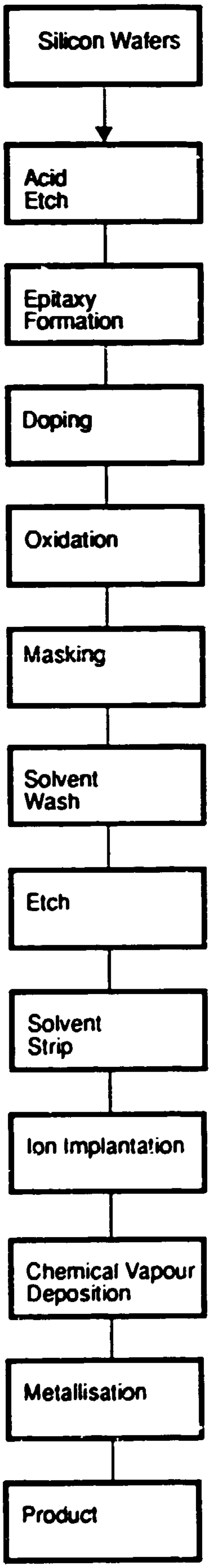
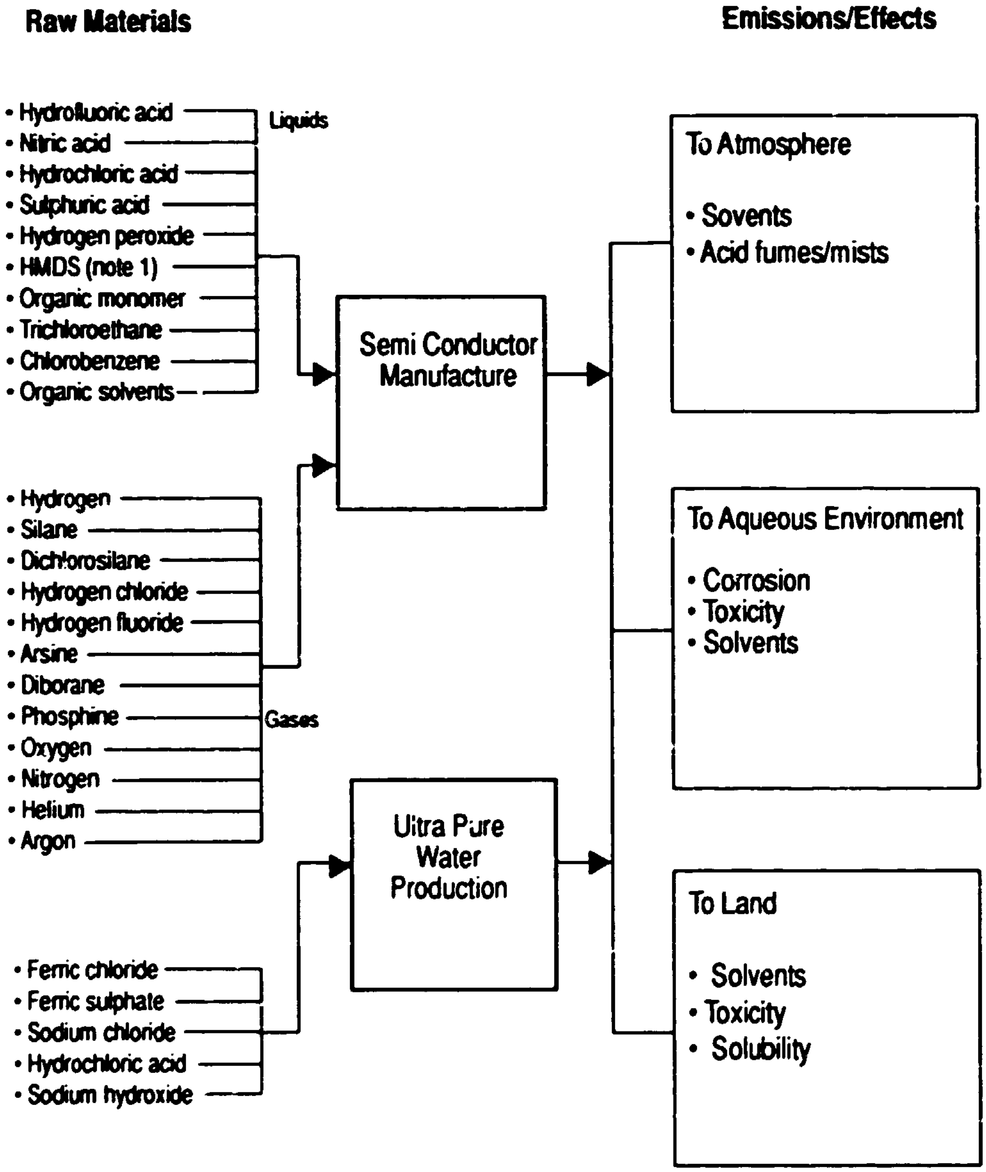
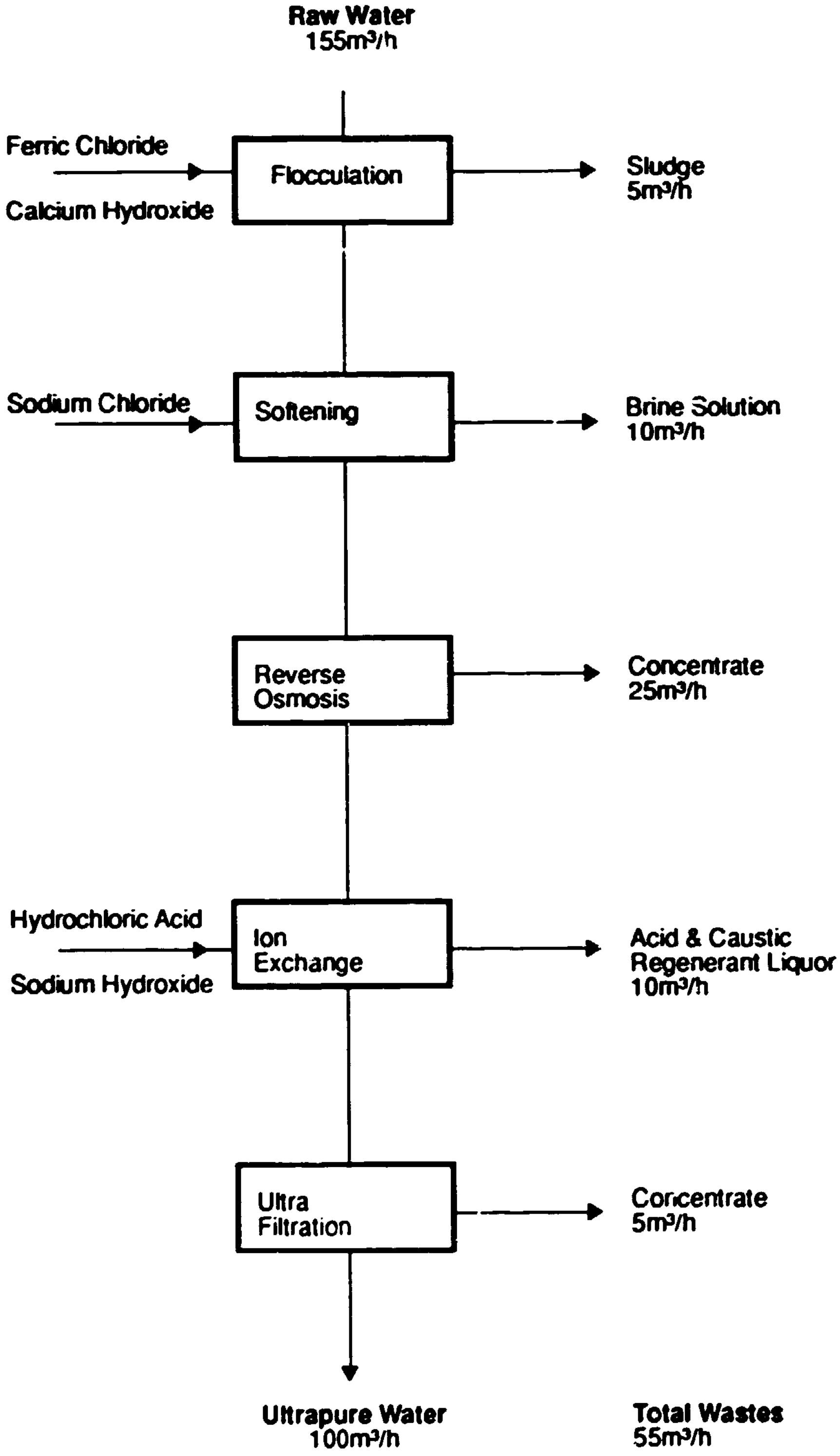


Figure 7.2 *Raw Materials and Emissions*
The Semiconductor Industry



Note 1: HMDS is Hexa Methyl Disalane

Figure 7.3 ***Production of Ultrapure Water***



8 *CONCLUSIONS*

The first paper attempts to define the extent of the pollution problem that arises from the use and generation of chemicals within the various industry types selected for study.

In most cases the potential environmental impacts of discharge of such chemicals to aqueous environment, to land or to atmosphere are significant.

Accordingly control of discharge is required and this can be achieved through end of pipe treatment processes alone, which is the high cost option, or through a combination of source control, to achieve an irreducible minimum of waste, and optimised end of pipe control.

Selection by industry of the latter combination approach will have positive benefits in relation to the costs of achieving effective pollution control; also it would allow industrial development to continue at an increased pace since long term growth otherwise would be hampered by environmental constraints.

Paper No 2 attempts to define a procedure by which effective pollution control can be achieved through a combination of source control and optimised end of pipe control.

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