An Investigation into the Water Management and Effluent Treatment in the Processing of

(i) pulp and paper (ii) Metals (iii) fermentation products and (iv) Pharmaceutical products.

By the
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Report to the

WATER RESEARCH COMMISSION

for the project

An investigation into the water management and effluent treatment in the processing of (i) Pulp and Paper, (ii) Metals, (iii) Fermentation Products and (iv) Pharmaceutical products.

PART II

Investigations into water management and effluent treatment in the South African Metal Finishing Industry.

106/2/87

Prepared for the

WATER RESEARCH COMMISSION

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ABSTRACT

A survey on water management and effluent treatment in the South African metal finishing industry was carried out for the Water Research Commission in order to collate existing knowledge on water and effluent problems and to formulate, on a co-ordinated basis, the scope for improved effluent treatment, water management and the disposal of effluents. A second objective of the project was to make recommendations to the Water Research Commission so that they could initiate, on a priority basis, research and development programmes for the solution of identified problems.

Literature surveys were prepared on the metal finishing industry, effluent treatment methods for this industry and the effluent discharge legislation as applied to this industry in South Africa, the United States of America, Canada and Europe.

A survey of municipalities and local authorities receiving metal finishing metal effluent was conducted by means of a questionnaire with the objectives of :-

(i) identifying and collating problems being associated by sewage works by the discharge of wastewaters containing heavy metals into sewage systems.
(ii) collecting basic data on sewage discharge by-laws and the acceptability of metal finishing into sewage works.
(iii) assessing the impact of the metal finishing effluents on sludge disposal techniques.

Individual metal finishing firms were contacted and basic information was collected on water usage, chemical usage, effluent characteristics, effluent treatment and conditions of discharge.

It was estimated that the water usage of 131 metal finishing firms was 8 800 Ml/year producing 6 800 Ml/year of effluent and 6 880 cubic metres of sludge. Some type of in-house effluent treatment system had been installed in 92 firms.

The following recommendations were made

(i) the volume of effluent should be reduced by in-house measures in that the metal load after conventional treatment by precipitation is proportional to effluent volume.

(ii) conventional effluent treatment processes (precipitation) is capable of achieving low concentrations of contaminants if complexing or chelating agents are absent. Encouragement should be given to the installation of innovative technology to enable metal finishing facilities to be isolated from the sewer systems.

(iii) consideration should be given to not only demonstrating existing and innovative technology but to the upgrading of existing facilities.

(iv) greater provision should be made for the provision of controlled dumping sites for potentially toxic sludges from the metal finishing industry.

INDEX (i)

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

ABBREVIATIONS

ac	alternating current
BAT	Best Available Technology Economically Achievable
BPT	Best Practical Technology Currently Available
Btu	British Thermal Unit
CA	Cellulose Acetate
CFMF	Cross-Flow Microfiltration
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
dc	direct current
DE	Department of the Environment (UK)
ED	Electrodialysis
EDR	Electrodialysis Reversal
EEC	European Economic Council
EPA	Environmental Protection Agency (USA)
HF	Hyperfiltration
NSPS	New Source Performance Standards
POTW	Pubicity Owned Treatment Works
PV	Permanganate Value
RO	Reverse Osmosis
SABS	South African Bureau of Standards
SSP	Soluble Sulphide Precipitation
SSSP	Slightly Soluble Sulphide Precipitation
TDS	Total Dissolved Solids
TFC	Thin Film Composite
UF	Ultrafiltration
UK	United Kingdom
USA	United States of America
WHO	World Health Organisation

INTRODUCTION

1. General

1.1 The Pollution Research Group, Department of Chemical Engineering of the University of Natal were appointed by the Water Research Commission in 1982 to investigate water usage, wastewater management, effluent reclamation and pollution control in the metal finishing industry within the Republic of South Africa.

2. Terms of Reference

The Terms of reference for the study were to :-

(i) collate the existing knowledge on water and effluent problems of the metal finishing industry.

(ii) survey water usage, chemical usage and effluent production within the metal finishing industry.

(iii) study the techniques of the metal finishing industry and the establishment of the quantity and quality of process streams to determine the scope for the recovery of water and by-products and possible methods of effluent treatment.

(iv) consider methods for the reduction of water intake, the internal recycling of water and in-house water and effluent management.

(v) assess the impact of advanced wastewater management techniques, including closed loop recycle systems.

(vi) formulate research and development priorities for consideration by a Coordinating Research and Development Committee for the metal finishing industry.

3. Method of Approach

3.1 A survey of Municipalities receiving metal finishing effluent was conducted by means of a questionnaire.
The main objectives of this survey were to

(i) identify and collate problems being experienced by sewage works by the discharge of wastewaters containing heavy metals into sewerage systems.

(ii) collect basic data on effluent discharge by-laws and the acceptability of metal finishing effluent into sewage works.

(iii) assess the impact of metal finishing effluent on sludge disposal techniques.

3.2 Individual metal finishing firms were contacted and basic information collected on water usage, finishing, chemical usage, effluent characteristics, effluent treatment and discharge point.

3.3 Literature surveys were prepared on the metal finishing industry, effluent treatment methods for this industry and effluent discharge legislation as applied to this industry of South Africa, USA, Canada and Europe.

CHAPTER 1. PLANNING FOR INDUSTRIAL WASTEWATER REUSE AND RECLAMATION

South Africa is a relatively arid country with an average rainfall of under 500 mm compared to a world average of 860 mm. The distribution of rainfall is uneven and about one third of the country receives an annual rainfall of less than 300 mm.

It is estimated that South Africa's total water credit is 34 000 million m^3/a. Present usage is 12 000 million m^3/a but demand is rising rapidly and projections indicate that supply and demand will be equal by the year 2020 (1).

The effective use of fresh water supplies is being impaired through quality deterioration brought about by the discharge of partially treated wastewaters and pollution from non-point sources. Industry, in general, discharges many substances which are resistant to degradation by conventional biological treatment and the self-purification processes of the water environment. Wastewaters containing intractable, toxic or carcinogenic substances should not be permitted to enter clean water supplies or water reclamation systems.

The Commission of Enquiry (2) into Water Matters estimated that 8 700 million m^3/a could be saved by improved utilisation of irrigation water (17%) and by water reclamation and reuse schemes (83%). The ratio of industrial to domestic water usage is about 60 : 40. For these reasons, it is evident that, in the future, industry has a major role to play in the South African water economy.

Water reclamation and reuse can be achieved in three main ways:-

(i) water recycling
(ii) reclamation of industrial wastewaters
(iii) reclamation of sewage for use in

- (a) irrigation
- (b) cooling systems
- (c) industrial use
- (d) potable supply systems

1.1 The Supply of Water to Industry

The Water Amendment Act of 1984 (3) makes provision for the intake quantities of public water for municipal, urban and industrial purposes, and the siting of industries using water, to be strictly controlled. The Act is administered by the Department of Environment Affairs, in consultation with the Department of Health and the South African Bureau of Standards, specialists in water science and research institutes.

These conditions can inter alia contain requirements in respect of the quality of effluent that may be discharged to municipal sewers and can also tripulate instructions for the reduction of specific water use. Failure to comply with any conditions of the permit could result, as a last resort, in the supply of water (regardless of source) to be suspended.

After a permit has been issued the permit holder is obliged to furnish the Department with details of actual water intake on a regular basis. In the event of new technology within a reasonable time.

In terms of Section 12 of the Water Amendment Act, 1984 any undertaking whose daily water intake from all sources (e.g. from public water supplies, boreholes on premisses, sea water and/or effluents received from other parties) exceeds 150 m^3 on any one day shall apply to the Minister for a permit to authorise such use (4). The Minister may issue the permit under such conditions as he considers necessary.

Water abstracted for industrial (including municipal) use must be returned as far as it is practically feasible, undiminished in quantity, to the stream of its origin after it has been purified to very stringent standards.

Embodied in the Water Amendment Act is the philosophy that :-

(i) purification of effluent is considered to be part of the industrial process, and
(ii) the industrial activities of the upstream user should not be to the detriment of the downstream user.

In this way it is endeavoured to obtain maximum use from the country's limited water resources.

1.2 Effluent Discharge by Industry

The disposal of industrial effluents may be managed by three main methods:-

(i) discharge to public streams
(ii) discharge to municipal sewers
(iii) industry based treatment and recycle

All discharges of effluents, whether permit holders or not, are obliged to submit regular reports on the quantity and quality of effluent discharged.

1.2.1 Discharge to Public Streams (Section 21 of the Water Amendment Act)

The purification of wastewater resulting from the use of water for industrial purposes is considered to be part of the industrial process.

All water seeping out or draining from land is considered as an effluent and has to comply with the quality standards (or exemptions) as the Minister may consider appropriate to grant in each instance. Any discharges into stormwater drains which can cause pollution of water are the responsibility of the local authority. The local authority and the discharger can be held jointly or separately responsible for such discharges. The irrigation or disposal to evaporation ponds is considered as a

temporary measure to isolate polluted effluent from the water environment. This method of disposal must be phased out with the 'best pacticable' means to treat those effluents to acceptable standards becomes available.

The standards that must be achieved for the discharge to public streams are prescribed by the Department of Environment Affairs and comprise :-

(i) a general standard
(ii) special standards for specified streams, specified areas and for specified industrial processes.

Table 1.1 summarises these discharge regulations.

TABLE 1.1 GENERAL AND SPECIAL STANDARDS FOR DISCHARGE, IN TERMS OF THE SOUTH AFRICAN WATER ACT, ACT NO. 54 OF 1956

Parameter	General Standard	Special Standard
Colour, odour, taste	nil	nil
pH	5,5 – 9,5	5,5 – 7,5
Dissolved Oxygen (%)	≤ 75	≤ 75
Temperature (°C)	≥ 35	≥ 25
Typical Faecal Coliforms (per 100 ml)	nil	nil
Chemical Oxygen Demand (mg/ℓ)	≥ 75	≥ 30
Oxygen Absorbed (mg/ℓ)	≥ 10	≥ 5
Total Dissolved Solids	≥ 500 mg/ℓ above intake	≥ 15% above intake
Suspended Solids (mg/ℓ)	≥ 25	≥ 10
Sodium (mg/ℓ)	≥ 90 above intake	≥ 50 above intake
Soap, oil, grease (mg/ℓ)	≥ 2,5	nil
Residual Chlorine – as Cl (mg/ℓ)	≥ 0,1	nil
Free and Saline ammonia – as N (mg/ℓ)	≥ 10	≥ 1
Nitrate – as N (mg/ℓ)	not specified	≥ 1,5
Arsenic (mg/ℓ)	≥ 0,5	≥ 0,1
Boron (mg/ℓ)	≥ 1,0	≥ 0,5
Chromium – total (mg/ℓ)	≥ 0,5	≥ 0,05
Copper (mg/ℓ)	≥ 1,0	≥ 0,02
Phenol (mg/ℓ)	≥ 0,1	≥ 0,01
Lead (mg/ℓ)	≥ 1,0	≥ 0,1
Copper (mg/ℓ)	≥ 0,5	≥ 0,02
Sulphides – as S (mg/ℓ)	≥ 1,0	≥ 0,05
Fluorine (mg/ℓ)	≥ 1,0	≥ 1,0
Zinc (mg/ℓ)	≥ 5,0	≥ 0,3
Phosphate – total as P (mg/ℓ)	not specified*	≥ 2,0**
Iron (mg/ℓ)	not specified	≥ 0,3
Manganese (mg/ℓ)	not specified	≥ 0,1
Cyanide – as CN (mg/ℓ	not specified	≥ 0,5

* In terms of Government Notice No. 7159 of 1 August 1980, effluents draining to certain sensitive areas must have soluble orthophosphate (as P) concentrations of less than 1,0 mg/ℓ

**In terms of Government Notice No. 7159 of 1 August 1980 this figure has been amended to not greater than 1 mg/ℓ of soluble orthophosphate (as P).

1.2.1.1 Exemption from Compliance

Section 21(5) of the Water Amendment Act covers the case where it would be impractical for an industry to purify its effluent to the prescribed standard.

On reciept of an application for exemption the Minister must give due consideration to :-

(i) the efficiency of internal house keeping.
(ii) the efficiency and operation of treatment systems available.
(iii) the availability of proven new technology.
(iv) the expected impact on the water environment should an exemption by granted.

After careful consideration, the Minister of Environment Affairs may grant permits of exemption from the standards and from the stipulation that water abstracted be returned to the stream of origin. The degree of exemption must be specified and the point of discharge must be such that no other person will be prejudically affected.

An exemption permit is subject to revision, modification or cancellation by a Water Court to whom any interested person may apply. The Minister may withdraw or amend the permit at any time by notice in writing to the permit holder.

1.2.1.2 Sea Discharges

Sea discharges are also covered by the provisions of the Sea Shore Act.

1.2.2 Discharge to Municipal Sewers

The municipalities may accept industrial effluents into their sewerage systems and sewage works. The responsibility for effluent purification and disposal then rests with the municipality. The municipal use of water is, under the terms of the Water Amendment Act, classed as an industrial use and hence all municipal discharges must comply with the relevant standards.

The municipalities promulgate their own discharge regulations (7) with which industry must comply and charge tariffs for accepting industrial effluent. Examples of municipal discharge regulations are given in Table 1.2.

TABLE 1.2 COMPARISON OF MUNICIPAL DRAINAGE REGULATIONS WITH WATER ACT 'GENERAL STANDARD'

	Water Act No. 54, 1956	City drainage by-laws			
	General Standards	Johannesburg	Pretoria	Durban	Cape Town
pH	5,5 – 9,5	> 6,0	6 – 10	> 6,0	5,5 – 12,0
Faecal coli	Nil	N.S.	N.S.	N.S.	N.S.
Dissolved O_2	> 75%	N.S	N.S.	N.S.	N.S.
Temperature	< 35 °C	N S.	N.S.	75°C	43 °C
Chemical oxygen demand (COD)	75	N.S.	5 000	N.S.	N.S.
4 h OA	10	1 400	200	N.S.	N.S.
TDS	Not increasing to more than 500 above intake	N.S.	2 000	N.S.	1 000 – 2 000
Electrical conductivity (mS/m)	N.S.	500	N.S.	N.S.	300 – 500
Suspendid solids	max. 25	N.S.	600	2 000	1 000
Sodium (as Na)	Not more than 90 above intake	N.S.	N.S.	N.S.	N.S.
Soap, oil and grease	max. 2,5	N.S.	400	50	400
Substances not in solution (incl. fat, oil, grease, waxes, etc.)	N.S.	2 000	N.S.	N.S.	N.S.
Substances soluble in petroleum ether	N.S	500	N.S.	N.S.	N.S.
Chlorides	N.S.	N.S.	N.S.	1 000	N.S.
Free Cl	max. 0,1	100	N.S.	N.S.	N.S.
Free and saline NH_3	10	N.S.	N.S.	N.S.	N.S.
Silver (as Ag)	N.S.	N.S.	Nil	N.S.	N.S.
Iron (as Fe)	N.S.	total concentration of all metals 50; individual metal 20	N.S.	N.S.	N.S.
Chromium (as Cr)	0,5		20	50	
Copper (as Cu)	1,0		20	50	
Nickel (as Ni)	N.S.		20	50	
Zinc (as Zu)	5,0		20	50	total not to exceed 50
Cadmium (as Cd)	N.S.		20	50	
Arsenic (as As)	0,5		N.S.	N.S.	
Boron (as B)	1,0	total of all metals 20; individual metal 5	N.S.	N.S.	
Lead (as Pb)	1,0		N.S.	N.S.	
Selenium (as Se)	N.S.		N.S.	N.S.	
Mercury (as Hg)	N.S.		N.S.	N.S.	
Sulphides (as S)	1,0	50	25	50	50
Fluorides (as F)	1,0	5	N.S.	N.S.	N.S.
Phenols	0,1	N.S.	N.S.	N.S.	N.S.
Formaldehyde	N.S	50	N.S.	N.S.	N.S.
Cyanides (as CN)	0,5	20	10	20	20
Total sugars and starch	N S.	1 500	N.S	1 500	1 500
Tar and tar oils not soluble in water	N S.	N.S.	60	60	60
Calcium carbide	N.S.	Nil	Nil	Nil	Nil
Total sulphates	N S.	1 800	300	200*	500

N S. = Not specified

*Sulphate in solution

The discharge regulations endeavour to ensure that the municipal sewage works are not overtaxed or put out of order. They are indicative of the amount of pretreatment required by industry to ensure treatability at the sewage works and allow compliance with the discharge standards.

The discharge of industrial effluents into municipal sewers does not exempt the discharger from the requirements of the Water Amendment Act in respect of the quality of the water discharged. This implies inter alia that the Minister may prescribe pretreatment of effluents before discharge to sewer.

1.2.3 Industry Based Recycling and Reclamation

Industry based reclamation and reuse of their wastewaters has the advantage that undesirable pollutants are not discharged into the water environment as they are removed at source. The wastewaters in a factory are fairly well-defined and being relatively concentrated, a wide range of separation techniques and treatment methods may be applied. In addition the recovery of process chemicals, by-products and heat energy is achievable in many instances.

Examples of industry based recycling and reclamation are:-

(i) direct reuse of non-contaminated process water; for example, cooling water to general factory use.

(ii) cascading of process water used on a high quality process to another process requiring only low quality water; for example, final rinses to first rinse operation.

(iii) treatment of a wastewater from one source for reuse in another process; for example, removal of suspended solids.

(iv) end-of-line mixed factory effluent treatment and reuse.

(v) closed loop treatment and recycle of wastewater from a particular source for direct reuse in the process. This is often accompanied by recovery of process chemicals, by-products and heat energy.

1.2.4 Future Trends

Municipalities planning sewage reclamation schemes will have to assess critically their industrial effluents in order to preclude those pollutants that are undesirable. In general it can be expected that municipal discharge regulations will be tightened especially with respect to colour, dissolved salts, heavy metals and intractable organic compounds.

In the future it can be expected that:-

(i) discharge conditions will become more strict,

(ii) exemption permits will be examined critically in the light of new technology,

(iii) new dams, water works, reticulation systems and sewage works will have to become self-financing resulting in higher charges for fresh water and effluent discharge.

In the longer term, the introduction of a Water Levy Act is being considered (5). This proposes that dischargers pay a levy based on the number of "harmfulness units" present in their annual discharge. The progressively increasing levy is aimed at providing an economic incentive to improve effluents and to facilitate long term economic planning.

CHAPTER 2. LITERATURE SURVEY - METAL FINISHING INDUSTRY

2.1 Introduction

Metal finishing is used to improve the surface of a base material by:-

- cleaning it
- hardening or softening it
- smoothing or roughing it
- depositing another metal on it by chemical exchange
- electroplating another metal or series of metals, on it
- converting its surface by chemical deposition
- coating it with organic materials
- oxidising it by electrolysis

These processes are known more familiarly as cleaning and pickling, annealing, case hardening, polishing, buffing, immersion plating, electroplating, phosphating, conversion coating, oxidising, painting, electropainting and anodising.

The corresponding changes produced by these methods of metal finishing on the base material serve to enhance the value of the treated item by providing such improvements as:-

- corrosion resistance
- durability
- esthetic appearance
- electrical conductivity

Such processes also fill many special engineering requirements of industry such as stress relief, ductility, heat resistance or the ability to stamp and form metal objects.

The metal finishing industry may be considered in three segments: large captive shops, small captive shops and job shops. The large captive shop is usually a divison of a major manufacturer whose

product requires metal finished products in quantity. These shops are to be found generally in the automative or appliance industries and are noteworthy by the size of their metal finishing facilities and magnitudes of their daily production and chemical consumption. The small captive shops are usually minor adjuncts to their parent industries. Their role is to supply metal finished incidentals to the principal products. The job shops exists solely on profits accrued from metal finishing. Jobs are accepted on contract and the shop must be prepared to serve a variety of industries. They are required to keep abreast of all changes in metal finishing technology and products' end use requirements.

2.2 Mechanical Processes (5)

2.2.1 Sand Blasting

Sand blasting, or more properly abrasive blasting, is a process where abrasive materials are directed at parts in order to clean them, give them a better finish, or otherwise change the surface characteristics. The wide range of abrasives used indicates that the method is no longer limited to the use of sand as an abrasive. The abrasives may be applied dry, either mechanically or by air, or wet in a slurry. The operation is generally carried out in a cabinet and will range from infrequent cleaning or honing of tools to very high volume production. The materials used for dry blasting will include steel shot; slag products; aluminium oxide; silicon carbide; natural products such as garnet and pumice; agricultural products, such as ground corn cobs; and glass beads. Dry blasting is usually preceded by a cleaning operation to prevent too frequent disposal of the abrasive. In wet blasting the abrasive is suspended in a slurry which will contain wetting agent, rust inhibitors, and anti-settling agents. As in dry blasting, pre-cleaning of the work pieces is usually done to minimize disposal frequency.

2.2.2 Tumbling

Tumbling or burnishing is a process performed by placing the work in a barrel and rotating it with or without abrasives, dry or wet. Its purposes are to deburr, descale, polish, burnish or to dry

production parts. Submerged tumbling barrels are perforated and rotate in an open tank containing water, wetting and cleaning agents. Disposal of this liquid with accumulated soil is necessary periodically, with the frequency dependent on production rates and amount of soil.

2.2.3 Vibratory Finishing

When the volume of production permits, or particular shape of finish demands it, vibratory finishing is used as a preference to tumbling. As with tumbling the work being finished may be plastic, rubber, metal or ceramic. Vibratory machines give an oscillating motion to the entire load which consists of the parts, abrasive media, water and chemical compounds. The media used in both tumbling and vibratory finishing including aluminium oxide; silicon carbide; steel balls, and other steel shapes; corundum, and other natural abrasives; granite; limestone; and quartzite. The liquids used in both tumbling and vibratory machines will vary in pH from 1 to 14. The acidic compounds are used for descaling or derusting. Alkaline liquids are used when metal removal by mechanical action is desired; neutral liquids are used when burnishng is required.

2.2.4 Polishing and Buffing

These processes, along with grinding, describe the operations performed on workpieces using wheels and abrasives. Grinding removes substantial quantities of material from the workpiece, polishing removes some material but leaves fine lines and buffing smooths the work and leaves a lustre. Grinding operations use hard fabricated wheels containing a variety of abrasives, both natural and synthetic. The operation generates particles of grit from the wheel as it wears metal from the workpiece. Polishing is performed by wheels made of muslin, canvas, felt, or leather. Abrasive grains are attached to the wheel by proprietary adhesives or hide glues. The most widely used abrasives for both polishing and grinding are aluminium oxide and silicon carbide. Some natural grits such as emery are used for specific purposes. Continuous belts made of woven cloth with factory applied abrasives are widely used with the belt running over a cushioned contact

wheel. Buffing wheels may be made of sisal, muslin, flannel, and occasionally wool. Chemical treatments are applied to the material to impart cutting characteristics or to increase wearability. Abrasives used include natural products such as tripoli and synthetic aluminium oxide and silicon carbide. In each of the above operations substantial exhaust systems are required and particles of abrasives, metal, cloth and lubricants are carried to cyclones or water scrubbers for removal. In the instance of scrubbers the resultant slurry must be discharged.

2.3 Physical Metal Coating (6)

Galvanizing or hot dip zinc coating is the most widely used physical process since it provides an inexpensive corrosion resistant surface. Aluminium coating of steel is finding increasing use, and lead and tin are also used. In all of these applications the metal is prepared by a cleaning processes that may include alkaline cleaners and will include hydrochloric and/or sulphuric acid for pickling and cleaning. A typical sequence for galvanising would be two 10% sulphuric acid dips, water rinse, zinc ammonium chloride flux dip and galvanize.

2.4 Non-Metallic Coating (6)

Painting is the most widely used metal finishing process and its application is well understood. The various preliminary cleaning and precoat processes are covered below under chemical processes. Plastic powder coatings have been finding increased usage and in many applications are replacing paint or metallic coatings. Preparation of the workpiece is similar to that for paint in its use of chemicals for cleaning and surface preparation. Each of these processes has potential disposal problems in materials retained by wash water spray booths.

2.5 Chemical Processes (6)

2.5.1 Chemical Cleaning

Vapour degreasing is a process used to remove soils soluble in a solvent and other foreign matter which may be entrapped but which will be loosened by the solvent and washed away by the liquid action as the vapour condenses. The solvents most frequently used are trichlorethylene, perchlorethylene, and methylene chloride.

The accumulation of soil necessitates periodic cleanout of sludge. If the volume is sufficient, the contaminated solvent may be recovered by distillation.

Four classes of soak cleaning can be used:-

(a) Emulsifiable solvents, emulsion cleaners and diphase cleaners are used to remove gross soil from the work. These contain petroleum or organic solvents. The operation is performed in tanks and the cleaners function by emulsifying and dissolving the solids, which settle to the bottom of the tank.

(b) Detergents which contain buffering salts, sequestering agents, dispersants, inhibitors, wetting agents and/or soaps are a second category of cleaners. Detergents wet, emulsify, disperse and solubilize the soil.

(c) Alkaline cleaners contain sodium hydroxide, silicates, and carbonates along with the dispersing agents and surface active agents.

(d) Acid cleaners are used to remove oil and metal oxides and to produce light phosphate coatings. They may be either inorganic or organic, such as phosphoric acid or gluconic acid. They are used with water miscible solvents and organic wetting and emulsifying agents.

Pickling is primarily used to remove scale, rust and solder from a variety of metals. Acids used include nitric, hydrochloric, hydrofluoric, sulphuric, chromic, acetic, and phosphoric acids. Inhibitors are frequently used to minimize attack on the metal. Concentrations will vary from 5% to 50% by volume. Scale loosening may be performed by solutions of potassium permanganate and caustic soda or soda ash followed by pickling.

2.5.2 Stripping of metallic coatings

This operation is used to salvage parts which have been rejected as a result of the faulty application of a finish. Chemicals are chosen which will remove the coating quickly with a minimum attack on the basic metal. Reverse electric current is frequently used in conjunction with the desired chemical.

Typical stripping baths include:

(a) Hydrochloric or sulphuric acid;
(b) Sodium hydroxide and sodium carbonate;
(c) Phosphoric acid with triethanolamine;
(d) Sodium cyanide and sodium hydroxide;
(e) Nitric acid;
(f) Phosphoric acid and chromic acid;
(g) Nitric acid and hydrofluoric acid.

2.5.3 Phosphating

Phosphating is a process designed to change a relatively unstable metallic surface into a stable, absorptive, non-metallic surface. The surface will also be non-conductive, an important factor in reducing corrosion.

The industrial applications are:

(a) To improve corrosion resistance under paint and to provide a superior bonding surface.

(d) To improve metal forming capability such as in extrusions, and to provide a base for lubricants.

(c) To improve the corrosion resistance of metals by providing a base for waxes and oils.

The basic chemicals used are zinc and iron phosphates with phosphoric acid. Manganese phosphates are occasionally used for extreme conditions. Concentrations vary from 5-10% by volume.

2.5.4 Chromating

Chromating is used on certain metals to produce a coating that is corrosion resistant, a good base for painting, or a decorative finish.

The bath is always acidic, containing hexavalent chromium compounds such as chromic acid plus organic or inorganic compounds which serve as activators or catalysts. The pH of the baths will range from less than 1 to 3. As the dissolved metal and trivalent chromium contamination increases it is periodically necessary under present technology to dispose of the bath. The frequency of disposal is influenced by the attention given to bath control.

2.5.5 Electroless plating

Immersion plating is the simplest form of electroless plating and the best known application is tinning. A great variety of household utensils are treated with this process and it is widely used industrially. Electroless plating may also take place by chemical reduction or auto-catalytic reduction. The latter process is now widely used in depositing a metal layer on plastic so that the part may be subsequently electroplated. Of the metals that may be deposited this way the largest application is with copper and nickel. In addition, copper is used as a deposit on circuit boards, and nickel on moulds or dies. In the latter case nickel imparts hardness, natural lubricity and anti-galling characteristics.

In the application of either copper or nickel as the substrate in the plating of plastics, a pre-plate procedure is required. This process includes the application of strong etchants, such as

chromic acid, acid neutralisers, catalysts and accelerators. The catalyst will most likely be palladium chloride and the accelerator a stannous chloride solution. The copper plating bath will probably be an alkaline copper nitrate with formaldehyde as a major component. The nickel bath will be nickel chloride with a hypophosphite and a glycollate and it will be strongly acid.

2.5.6 Bright Dipping

Bright dipping is a special application of pickling, performed on aluminium, cadmium, copper, steel, zinc and stainless steel. Because of the vigorous chemical action of pickling and bright dipping, a heavy metal load accumulates in the baths and periodic disposal is required.

Mild acid baths with a concentration of 5% or less are used for light etching to improve adhesion of coatings and for surface activation.

2.5.7 Metal Colouring

A wide variety of colouring effects are obtained on metals by using dips, e.g., antiqueing and the blueing of gun barrels

Most of the antiqueing effects are obtained from alkaline sulphide solutions and thiosulphates. One formula for gun blueing contains copper sulphate, mercuric chloride, ferric chloride, nitric acid and denatured alcohol.

If present in any quantity in an effluent the sulphides may interfere with waste treatment.

2.6 Electrolytic Processes (6)

2.6.1 Electrocleaning

Electrocleaning is a process used as a final preparation of parts after heavy soil has been removed by any of the cleaning processes mentioned above. The operation takes place in a heavy duty alkaline solution and the work may be anodic, cathodic or alternating between each condition. As in all the electrochemical processes that will be described the electrical source will be direct current at relatively low voltages and high amperages. The function of electrocleaning is to remove remaining soil and to make the surface chemically active.

2.6.2 Anodizing

Anodizing is a process used to produce an oxide on a metal in a controlled manner. Its purpose is to give the base metal a corrosion resistant surface with some capability for resisting abrasion. It will also present a surface capable of accepting other finishes and, particularly in the case of aluminium, for accepting dyes. While some limited anodizing is performed on zinc, by far the greatest amount is done on aluminium. For alloys of aluminium with less than 5% copper the operation will take place in a chromic acid solution and for those with more than 5% copper it will take place in sulphuric acid. A typical chromic acid bath will have 50 - 100 g/l of chromic acid with some chloride and sulphate ions present. A sulphuric acid bath will have 15-20% sulphuric acid. The work is anodic and the anodizing may be followed by a sealing bath containing 45 g/l sodium dichromate. A typical process sequence for anodizing might be: vapour or alkaline soak degreasing - electroclean - acid dip - electropolish - or chemical polish - anodise and seal; with appropriate rinsing between each stage. The chemical polish will be 85% phosphoric and 15% nitric acid.

2.6.3 Electroplating

Electroplating is the electro-deposition of an adherent metallic coating upon an electrode, which is the workpiece, for the purpose of obtaining a surface with properties or dimensions different from those of the basic metal. These properties may include improvement of appearance, corrosion protection, wear resistance, etc. The operation takes place in aqueous solutions containing the metal ion to be plated. The work piece is cathodic and in most instances the metal ion is constantly replenished from an anode containing the metal. A notable exception is chromium where the anode is insoluble and metal ions are replenished by additions of chromic acid.

Electroplating must be preceded by cleaning and activating operations and a typical sequence would be:

(a) vapour degrease or soak clean in an emulsion or detergent cleaner
(b) spray clean in a detergent cleaner
(c) electroclean in an alkaline cleaner
(d) sulphuric acid dip
(e) electroplate
(f) electroclean
(g) sulphuric acid dip
(h) second electroplate

Rinsing would follow each process stage except (a).

There may be a single electroplate only and it may or may not be followed by a chemical dip such as sodium dichromate or an oxidising agent. The former would be most likely on zinc or cadium and the latter on copper or brass. Additional layers of electroplate may also be applied. For example in the plating of zinc die castings, two layers of copper, and one or two layers of nickel and chromium are applied.

Typical acid plating baths are shown below in Table 2.1.

TABLE 2.1 Typical Acid Plating Baths (6)

	Chromium	Copper 1	Nickel	Copper 2	Zinc 1	Zinc 2	Tin
Chromic Acid	200						
Sulphuric Acid	1,5	60					55
Metal Sulphate		200	350		180		40
Metal Chloride			45			140	
Copper Flouborate				350			
Boric Acid			40				
Phenol Sulphonic Acid							40
Sodium Acetate					45		
Aluminium chloride						25	
Sodium Chloride						250	
Brightener		organic	organic				
Temperature °C	40-50	room	45-60	20-50	25-50	room	

(concentrations expressed in g/l)

The following notes apply to acid plating baths:-

(a) the above chromic acid bath would contain traces of fluoride and some baths may be operated with up to 400 g/l chromic acid.

(b) black chromium is finding increasing application for non-reflecting surfaces and for this acetic acid is used in a 1:1 ratio with chromic acid.

(c) hard chromium plating differs from decorative plating only in the thickness of the plate. In order to impart this hardness over softer metals, the thickness must be over 0,04 mm.

(d) acid copper plating is finding increasing use as new developments improving levelling action make it useful in plating unbuffed plastic and other parts.

(e) the brighteners used in nickel plating impart the appearance characteristics and grain structure of the deposit. While low in concentration, their organic nature may interfere with a waste treatment or recovery system.

(f) nickel is also plated from a sulphamate bath where control of internal stress and fatigue is important.

(g) nickel plating is one of the most widely used and is most often found as part of a multi-layer system. It has the combined characteristics of hardness, appearance and corrosion resistance.

(h) zinc plated from cyanide baths has a better appearance than that plated from acid baths, but the acid bath is cheaper to operate. Sulphate baths are used to plate on malleable iron and strip steel. Chloride and alkaline baths are now on the market. They give a good appearance and are being offered as substitutes for cyanide zinc plating.

(i) tin plating from acid baths finds its main application in strip and wire plating.

Typical cyanide plating baths are shown in Table 2.2.

TABLE 2.2 Cyanide Plating Baths (6)

	Low CN					High Speed		
	Zinc	Zinc	Cadmium	Copper 1	Copper 2	Gold	Silver	Tin
Metal Cyanide	75	12		25	75	2	75	
Cadmium Oxide			22					
Sodium Hydroxide	110	90	15	4	30			
Potassium Hydroxide							3	25
Rochelle Salt				45				
Sodium Carbonate			30-75					
Potassium Carbonate							15	
Potassium Stannate								400
Tin Metal								160
Polysulphide			1					
Sodium Cyanide	40	4	80	35	100			
Potassium Cyanide						7	90	
Brighteners	Org./ Met.	Org./ Met.	Org./ Met.	Organic	Organic	Dipot Phos		
Temperature °C	Room	Room	Room	60	60	65	35-50	80

(concentrations expressed in g/l)

The following notes apply to cyanide plating baths:

(a) zinc plating from cyanide baths is one of the most used plating operations. While it is primarily used for corrosion protection, post-plating treatments can produce a decorative appearance.

(b) low cyanide baths require more care in operation.

(c) Cadmium, while more expensive than zinc is used where superior corrosion protection is required. Improvements in the corrosion resistance of zinc and the use of chemical treatment systems has, in some cases, made cadmium plating unnecessary, since equivalent corrosion protection can be provided.

(d) cadmium has not lent itself readily to low cyanide formulations.

(e) copper plating from cyanide baths is always used in plating zinc die castings.

(f) the two formulations of copper, (1) and (2) above, are frequently found in successive baths with no rinse between.

(g) brass plating is a mixture of zinc and copper solutions. Cyanide levels tend to be higher.

(h) gold's application as a decorative plate is well known and the formulation shown is for this type. Industrial uses are increasing rapidly and production line techniques are being introduced.

(i) silver is also finding increasing industrial application in the electronics field.

Zinc is also plated from alkaline non-cyanide baths. This process has not widely replaced the traditional cyanide baths because of

the greater difficulty in cleaning, especially in older facilities.

Copper is plated from pyrophosphate baths as a substitute for the higher concentration cyanide copper bath.

2.6.4 Electropolishing

This process, which is the reverse of plating, removes metal from the working surface. The effect is to smooth and brighten the surface and in some applications it is used for deburring.

Baths contain a variety of chemicals, depending on the metal being polished and the desired effect.

The bath may contain any of the following chemicals:

(a) Fluoboric acid (Alzac process on aluminium)
(b) Sulphuric and hydrofluoric acid
(c) Phosphoric acid
(d) Chromic acid
(e) Arsenic acid
(f) Tri-sodium phosphate
(g) Ammonium phosphate
(h) Nickal sulphate
(i) Hydrochloric acid and glycerine

2.6.5 Electrocoating

Electrocoating or electrophoresis is a process in which an organic coating is deposited electrolytically. When dc current is applied in a bath where the work is cathodic there is a migration of pigment and resin particles to the part. The excess paint is washed from the surface of the part as in other chemical treatments. Paints used will include 8-10% solids, surfactants and possibly organic solvents. The pH will be between 7 and 10.

2.6.6 Electroforming

Electroforming is a process using plating solutions to deposit a layer of metal of such thickness as to have structural strength of

its own. It is used for paint masks and other applications where a configuration must be closely followed.

2.6.7 Composition and Lifetime of Plating Baths

Tables 2.3 to 2.7 (27) indicate the nature and range of metals and other toxic substances in plating solutions. Where the acid radicals are not toxic, only the metal concentrations are given. In Table 2.3 the concentration of cyanide is expressed as CN and includes both simple and complex cyanide. Chromium plating solutions (Table 2.4) contain hexavalent chrome (chromic acid) and catylists (sulphuric acid and sodium fluosilicate). Acid plating solutions (Table 2.5) are based principally on sulphates or chlorides. The free acid concentrations are indicated where they are high. Fluoborate based solutions (Table 2.6), are used for depositing cadmium, copper, lead, nickel, tin, zinc and a number of alloys. These solutions are only used for special purposes. The composition of acid anodising baths is given in Table 2.7, they are all very acidic.

Certain concentrated bath have limited lifetime and must be discarded periodically (Table 2.8). Procedures are available (18) to clean most contaminated plating solutions.

TABLE 2.3 Cyanide-Based Solutions (7)

Plating Solutions	General range of concentration of	
	Total cyanide as g/l CN	metal in g/l
Copper	15 to 52	7 to 40
Zinc	4 to 64	8 to 50
Cadmium	20 to 67	15 to 25
Silver	12 to 60	13 to 45
Brass	16 to 48	Cu 6 to 25 Zn 2 to 13
Bronze	40 to 40	Cu 30 to 35 Sn 15 to 20
Tin-Zinc	12 to 18	Sn 25 to 30 Zn 1 to 2

TABLE 2.4 Chromium-Plating Solutions (7)

Type of solution	Concentration in g/l	
	Chromic acid	as Cr
Bright chromium-plating	192 to 520	100 to 270
Hard chromium-plating	270 to 308	140 to 160

TABLE 2.5 Acid-Plating Solutions (7)

Plating solution	General range of concentration of	
	free acid as H_2SO_4 in g/l	metal in g/l
Copper	45 to 55	50 to 52
Zinc		70 to 80
Nickel		40 to 90
Tin	60 to 138	21 to 34
Zinc chloride		131 to 145

TABLE 2.6 Fluoborate-Based Solutions (7)

Type of solution	General range of concentration of	
	fluoborate as BF_4 in g/l	metal in g/l
Tin	160 to 210	75 to 85
Lead	125 to 184	90 to 100
Tin-lead	125 to 150	Sn 7 to 60 Pb 25 to 88
Zinc	255 to 265	80 to 85

TABLE 2.7 Typical Anodizing Solutions (7)

Constituent	Concentration
Sulphuric acid (H_2SO_4)	100 to 275 g/l
or Oxalic acid ($H_2C_2O_4$)	30 to 100 g/l
or Chromic acid (as CrO_3)	80 to 100 g/l
Chlorides (as Cl^-)	max. 20 mg/l
Aluminium, dissolved (as Al)	max. 15 to 18 g/l

TABLE 2.8 Typical Lifetimes of Cconcentrated Plating Solutions (7)

Bath	Life	Comments
Alkaline cleaners	4-6 weeks	cyanides could be present
Chromic/Nitric Acid Passivation of Galvanising	2-3 weeks	
Acid dip (Zinc die castings)	1-2 months	2-4 g/l Zn
Zinc and Copper Cyanide	up to 25 years	failure to remove carbonates will reduce bath life
Chromic acid Plating solutions	up to 25 years	the following contaminants will reduce life if not removed :- reducing agents, foreign cations (Fe, Zn etc) chlorides and sulphates
Nickel	up to 25 years	can be cleaned
Anodising baths	depends on application	life determined by aluminium limit of 12 to 45 g/l

2.7 Effluent Sources and Characteristics (9)

Contaminants in the effluent from electroplating shops originate in several ways. The most obvious source of pollution is the drag-out of various processing baths into subsequent rinses. The amount of pollutants contributed by drag-out is a function of such factors as the design of the racks or barrels carrying the parts to be plated, the shape of the parts, plating procedures and several interrelated parameters of the process solution, including concentration of toxic chemicals, temperature, viscosity and surface tension.

With conventional rinsing tehniques, drag-out losses from process solutions result in large volumes of rinse water contaminated with relatively dilute concentrations of cyanide and metals. Rinse waters that follow plating solutions typically contain 15 mg/l to 100 mg/l of the metal being plated (Table 2.9).

Most job shops operate several plating lines that contain different types of cleaning and electroplating baths, such as zinc, copper, nickel, cadmium and chromium. The combined rinse waters dilute the concentrations of individual metals, usually to less than 50 mg/l. The results of a survey of effluent from 22 electroplaters in the Cleveland (USA) area are presented in Table 2.10 (10).

The WHO (11) have issued the following guidelines (Table 2.11 and Table 2.12) for calculating the effluent from electroplating installations.

Another source of effluent contamination is discarded process solutions. These solutions are primarily spend alkaline and acid cleaners used for surface preparation of parts before electroplating. The solutions are not usually made up of metals, however, there are a few cleaners that contain cyanide. Plating baths and other process solutions containing high metal concentrations, such as chromate solutions, are rarely discarded.

TABLE 2.9 Principal Constituents and Concentrations in the Untreated Effluent from Metal Finishing Processes (6)

Constituent	Plating on steel	Plating on Zinc	Plating on Brass	Plating on Plastics	Anodising	Conc mg/l
Fe^{2+}	x					1 - 10
Cu^{2+}	x	x	x	x		5 - 50
Ni^{2+}	x	x	x	x	x	2 - 15
Cr^{6+}	x	x	x	x	x	10 - 120
Cr^{3+}	x	x	x	x	x	0,1 - 1,0
Zn^{2+}	x	x				10 - 50
Cd^{2+}	x					10 - 50
Sn^{2+}	x			x		0,1 - 20
CN^{-1}	x	x	x			1 - 50
SO_4^{-2}	x	x	x	x	x	15 - 25
Cl^{-1}	x	x	x			1 - 250
CO_3^{-2}	x	x	x	x		10 - 50
SiO_3^{-2}	x	x	x	x		30 - 50
PO_4^{-3}	x	x	x		x	20 - 50
Organics	x	x	x	x		0,1 - 1,0

TABLE 2.10 Effluent Characteristics of 22 Cleveland (USA) Electroplating Shops (12)

Pollutant	Effluent concentration (mg/l)		
	Minimum	Maximum	Average
Cyanide, total	0,1	95,9	14,4
Copper	0,1	47,2	4,7
Nickel	0,1	52,2	5,7
Chromium, total	0,1	178,0	20,2
Zinc	0,4	101,4	19,3
Lead	0,1	3,0	0,4
Cadmium	0,1	24,3	4,3

TABLE 2.11 Raw Waste Calculation from Quantity of Anode Used (11)

	Waste Volume	Waste Mass
	m^3/ton metal plated	kg/ton metal plated
Cu	1 403	9,77 Cu and 20 CN(1)
Ni	1 519	3,98 Ni
Cr_2O_3	36 300	743 Cr(total) and 297 Cr^{6+}
Zn	1 815	224 Zn and 32,5 CN
Cd	883	Unknown Cd and 12,7 CN
Sn	1 125	Unknown Sn

(1) if a cyanide bath is used

TABLE 2.12 Effluent Production based on Electricity Consumed or Area Plated (11)

Bath	Waste Volume (m^3/Amp-h)	Dry Waste (mg/Amp-h)	Waste Volume (m^3/m^2 plated)	Dry Waste (mg/m^2 plated)
Copper	1,67	11,6	94	658
Nickel	1,66	4,35	103	270
Chrome	1,66	13,6 Cr^{+6} + 34 Cr (total)	95 93	918 Cr^{+6} + 1 946 total Cr
Zinc	1,52	205		
Cyanide (any metal)		23,8		1 333

The amount of pollutants contributed to the total pollution load by discarded process solutions varies considerably among plating shops. It is not uncommon to find cyanide and heavy metals in concentrations of several thousand milligrams per liter of spend solutions. This contamination is caused by drag-in from previous process cycles and attack of the basic metals by the chemicals in the cleaning solutions. Tables 2.13, 2.14 and 2.15 presents an analysis of typical process solutions.

TABLE 2.13 Analysis of Typical Process Solutions that are Dumped Periodically (12)

Pollutant or Parameter	Alkaline Cleaner			Electrocleaner	Acid Dip		
	1	2	3		1	2	3
Volume (kl)	1,26	1,35	1,32	1,52	0,25	0,20	0,64
Cyanide, total (mg/l)	2,5	85,5	2,8	1,3			
Cadmium (mg/l)	0,2	2,6	0,4	0,8	6,4	0,1	1 990,0
Chromium, total (mg/l)	40,0		0,1	36,5	39,2	10,8	
Copper (mg/l)	58,1	19,4	10,9	1,9	12,1	0,1	
Nickel (mg/l)	6,9	0,9	0,3	5,2	128,0	0,6	
Lead (mg/l)	4,4		0,7	1,9	11,6	0,1	
Zinc (mg/l)	1,2	74,0	162,0	10,5	365,0	5 240,0	

TABLE 2.14 Composition of Raw Waste Stream from Common Metal Plating (12)

Constituent	Range (mg/l)
Copper	0,032 - 272,5
Nickel	0,019 - 2 954
Chromium	
Total	0,088 - 526
Hexavalent	0,005 - 335
Zinc	0,112 - 252
Cyanide	
Total	0,005 - 150
Amenable to chlorination	0,003 - 130
Fluorides	0,022 - 142
Cadmium	0,007 - 21,6
Lead	0,663 - 25,4
Iron	0,41 - 1 482
Tin	0,060 - 103
Phosphorous	0,020 - 144
Total Suspended Solids	0,100 - 9 970

TABLE 2.15 Aluminium Anodising - Effluent Analysis (13)

Total solids	1 200 - 2 500
Suspended solids	150 - 890
Zinc	0,07 - 0,18
Aluminium	180 - 200
COD	17 - 35
Chloride	22 - 48
Iron	2 - 46
Sulphate	93 - 5 200

All values in mg/l

Accidental spills, leaks and drips of process solutions also can contribute significantly to effluent contamination. The plating room usually is laid out so that the entire area drains on the floor, which is only an extension of the sewer system leaving the facility. Although it is not common for a tank to spring a leak that would allow the entire solution to leak away undetected, a slow leak amounting to a solution loss of 38 to 76 l/d could go undetected for months in many shops. Also, it is not unusual to compensate for evaporation losses in a process tank by adding water to a process solution with an unattended hose that causes overflow of the solution to the floor drains.

In some shops, the dropping of plated parts is a significant source of pollution. Process solution tanks and rinse tanks often are separated by a distance of several meters or more. Carrying the racks of parts between tanks will cause plating solution or drag-out to drip on the floor and enter the drain system.

Other sources of contaminants from electroplating shops exist ; however, they are not as universally present as the preceding waste sources. Additional pollution sources include sludges from the bottom of plating baths generated during chemical purification, backwash from plating tank filter systems, and stripping solutions.

The percentage contributed by each pollution source to the pollutant concentration of the final effluent can vary substantially among electroplating shops. For shops whose primary process is chrome plating (copper-nickel-chromium), drag-out usually will be the major cause of metal loss. At facilities that engage in large nickel plating operations, more nickel is lost from the operation of the chemical purification filters and through the discharge of sludge from the bottom of tanks after purification of the plating solution than through normal drag-out. The main contribution to the effluent metal concentration in zinc or cadmium plating is the metal that is either stripped off the danglers or crack tips in the acid dip step of the cleaning cycle or removed from the work in dichromating.

Although some shops may have a higher contribution of pollutants from other sources, in almost every case, the most significant pollution problem is drag-out and the resultant contaminated rinse water. The size and cost of pollution control equipment depend primarily on wastewater volumetric flow rate. Because the volumes of rinse water are overwhelmingly larger than the volumes of all other waste sources, it follows that contaminated rinse water is the major source of pollution. A survey in Cleveland showed that the average rate of rinse water discharged from 22 electroplating shops was 70 000 l/d, whereas spent process solution accounted for only 230 l/d (10).

Electroplating shops should concentrate on drag-out and rinse waters during the planning stages of pollution control.

The amount of metal sludges produced after precipitation by sodium hydroxide are given in Table 2.16 (14).

TABLE 2.16 Sludge Generated and Sludge Disposal Volume for Electroplating Waste Treatment System (14)

Waste Metal Components	Dry Solids kg/kg metal precipitated	Sludge (gal/lb metal precipitated)	
		Generated 3% solids	Dewatered 25% solids
Aluminium	2,89	11,2	1,14
Cadminium	1,30	5,0	0,51
Chromium	1,98	7,7	0,79
Copper	1,53	5,9	0,60
Iron	1,61	6,2	0,63
Nickel	1,58	6,1	0,62
Zinc	1,52	5,9	0,60

Using sodium hydroxide

CHAPTER 3. LITERATURE SURVEY - EFFLUENT TREATMENT PROCESSES

3.1 Conventional Method

The effluent can be divided into two classifications for treatment

(a) continuous flows - all rinses, small swills and washes
(b) periodic dumps - process solution dumps, filter cleaning and ion exchange regeneration.

All effluent streams that are of a relatively high concentration or are discharged at high rates should be stored in buffer tanks prior to pretreatment or gradual discharge into the final treatment system.

Individual effluents are segregated (Figure 3.1) and certain streams are pretreated prior to release to the final precipitation plant.

(a) non toxic rinses and washes flow directly to the final treatment plant
(b) non toxic dumps are released at a controlled rate to the final treatment plant.
(c) toxic dumps and rinses are pretreated prior to controlled release to the final treatment plant.

The Best Practical Technology (BPT) for the treatment of metal finishing effluent (15) consists of :-

segregation and destruction of oxidisable cyanide,
segregation and reduction of hexavalent chrome,
equalisation of the different streams and precipitation of the metals
settling of suspended solids
separation and disposal of the sludges.

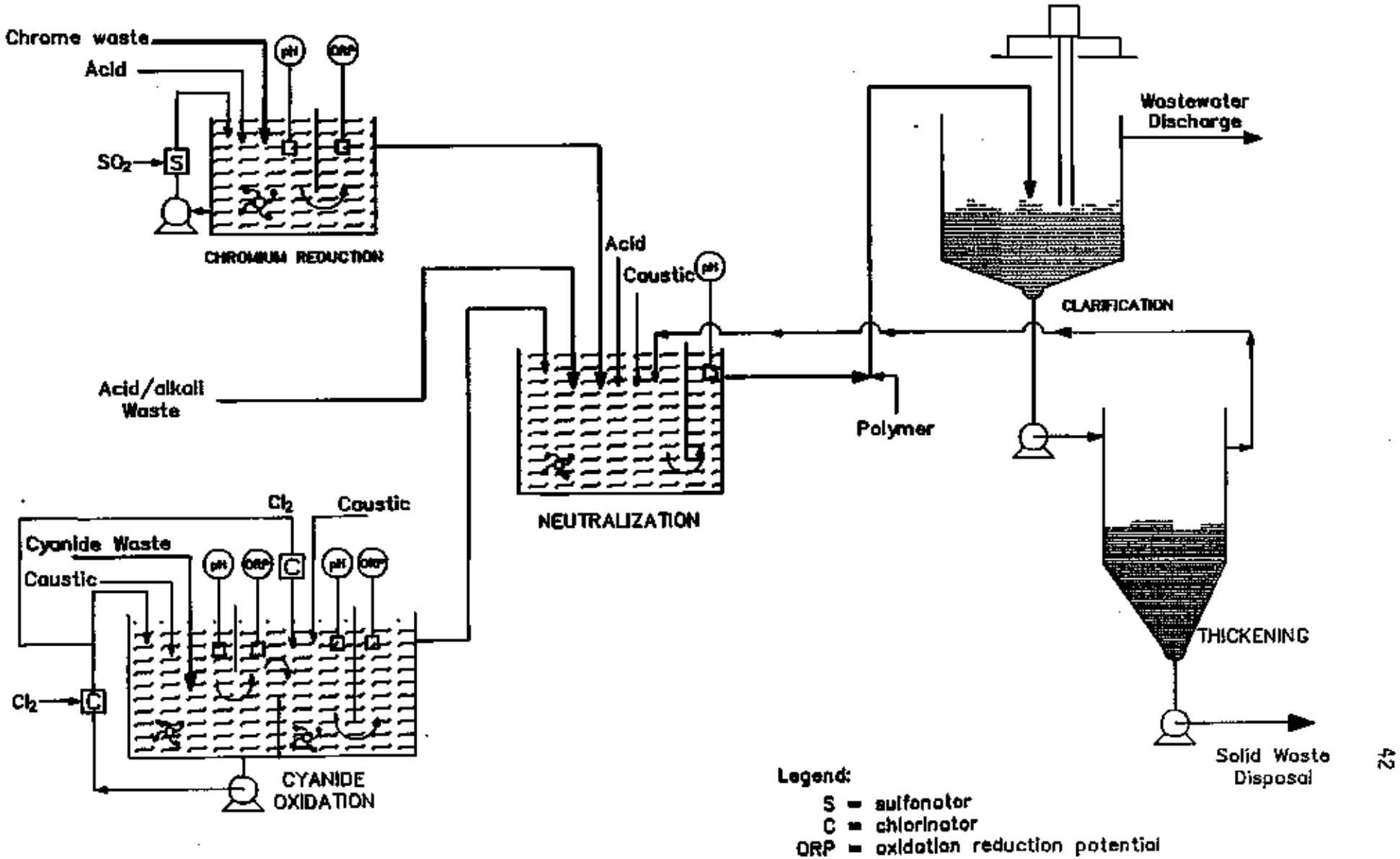


Figure 3.1 : *Electroplating Industry Conventional Wastewater Treatment*

Metals and other contaminants in the supernatant and final effluent are expected to be at or below the levels shown in Table 3.1 (15, 16 and 17).

The current trend towards chelating agents and the more extensive use of brighteners has resulted in the need for alternative effluent treatment systems in order to reduce heavy metal concentrations to acceptable limits.

TABLE 3.1 Expected Levels of Contaminants in Final Effluent after Chemical Treatment (17)

pH	6,0 - 9,5	
Total Suspended Solids	20 - 50	
	Total (dissolved and undissolved)	Dissolved
Cd	1,5	0,2
Cr+6	0,5	0,1
Cr (total)	1,0	0,5
Cu	1,0	0,5
Ni	2,0	1,0
Pb	1,5	0,5
Zn	2,0	1,0
Fe	2,0	1,0
CN (oxidisable)	0,1	0,1
CN (total)	1,0	0,1

All values except pH, in mg/l

3.1.1 Rinsing and Drag-out Control

The size and cost of pollution control equipment depends primarily on wastewater volumetric flowrate. Rinse water flows are much greater than any other effluent source in a plating factory.

In addition, the plating solution entering the rinse tanks in many cases can represent as much as 50 - 90% of the plating solution consumed in the plating process. The concentration of the dragout entering the first rinse tank is identical to the plating bath solution. Consequently the reduction of drag-out and rinse water usage is the first phase in the installation of any effluent treatment system.

Typical figures of dragout associated with different shapes and draining times are given in Table 3.2 below:

TABLE 3.2 Plating Drag-Out (8)

	ml/m2
Vertical parts ; well drained	15
Vertical parts ; poorly drained	80
Vertical parts ; very poorly drained	160
Horizontal parts; well drained	30
Horizontal parts; very poorly drained	400
Cup shaped parts; very poorly drained	325-1000

Assuming good rinsing efficiency, the concentration of dragout from a rinse tank is the same as the concentration of rinse water in that tank. The concentration of dragout can be decreased satisfactorily using one rinse tank and a high rinse water flow rate; however additional rinse tanks are usually included to reduce the quantity of rinse water used.

The volume of rinse water will depend on many factors, such as volume and concentration of dragout, number of counter-current rinse tanks, rinsing efficiency and the final concentration of plating chemicals permissible on the product after rinsing. Usually the concentration of plating chemicals adhering to the work piece after final rinsing will be in the range 5 to 50 mg/l, although some plating operations require final concentrations of dissolved solids as low as 1 mg/l. Typical concentrations of total dissolved solids in final rinses are 16 mg/l for chrome plating, 45 mg/l for nickel plating and 50 mg/l for cyanide plating.

The arrangement and number of rinse tanks is usually dependent on economics and space limitations. Typically, one to five rinse tanks are used. For a given number of rinse tanks, a counter current rinse system will minimise the consumption of rinse water. In this arrangement, the first rinse tank has the highest concentration of plating chemicals.

The ratio of rinse water volumetric flow rate to dragout volumetric flow rate is defined as the rinse ratio (r). The relationship between the number of rinse tanks, the rinse ratio and the resultant dilution in the rinse tanks is (8, 29) :-

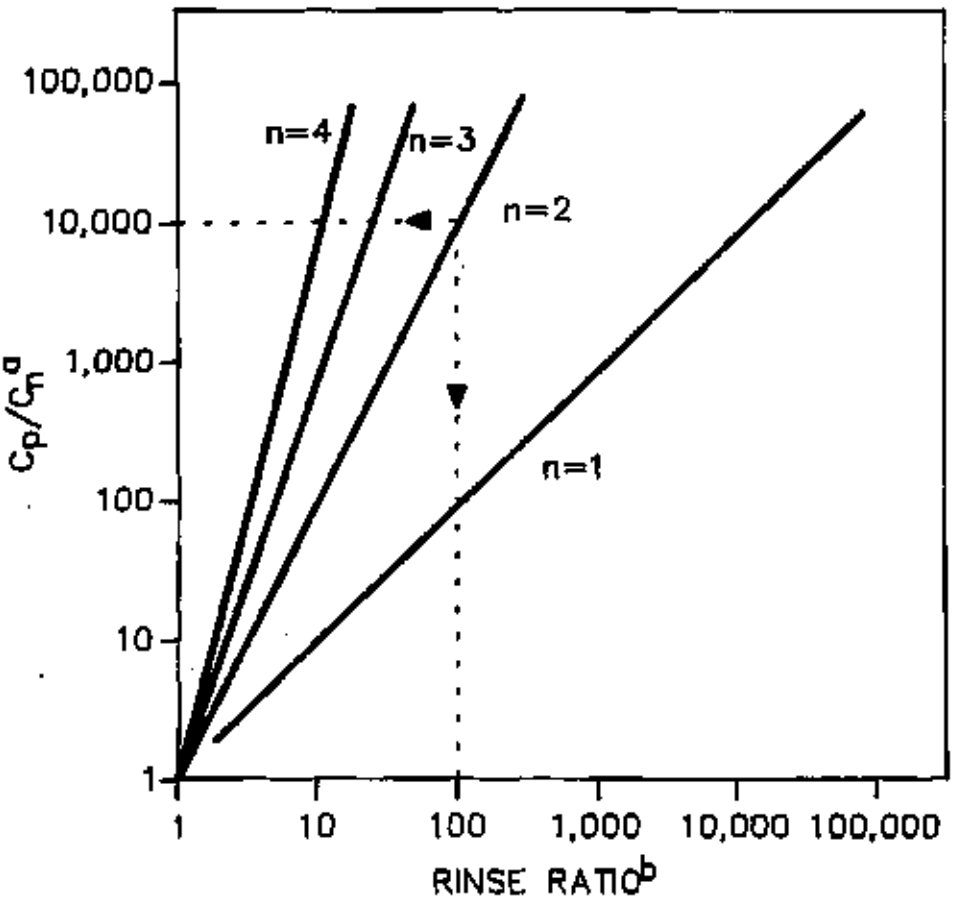
$$r = \left[\frac{C_p}{C_n}\right]^{\frac{1}{n}} \qquad (1)$$

Where
- n number of rinse tanks
- C_p plating bath concentration
- C_n concentration in the last rinse bath
- r rinse ratio

This relationship is shown in Figure 3.2 which also shows the potential recovery of dragout chemicals if the rinse water were to be recycled.

The percentage potential recovery is given by :-

$$\text{percentage potential recovery} = \left[1 - \frac{C_n}{C_p}\right] \times 100 \qquad (2)$$



[a] C_n = concentration in final rinse;
C_p = concentration in process bath;
n = number of rinse tanks.

[b] Rinse ratio=gal rinse water/gal drag-out.

Note.—This graph shows rinse ratios for countercurrent rinse systems. For series rinse systems, multiply the rinse ratio for a countercurrent arrangement with the same number of tanks, e.g., two-stage countercurrent rinse with $C_p/C_n = 10^4$ has a rinse ratio of 100 gal/gal. But, with the two-stage series the required rinse ratio is 100 X 2 = 200 (gal rinse water/gal drag-out).

Figure 3.2 : *Estimating Rinse Ratios Based on Drag-Out and Final Rinse Concentration for Multiple-Tank Rinse Systems*

The different levels of potential chemical recovery over a range of rinse ratios and for one and two counter rinse tanks is shown in Figure 3.3. For example, if chemical recovery were from one rinse tank only and the rinse ratio were 10 then the potential plating chemicals that could be recovered is 90%. If the rinse ratio were to be raised to 40 only an additional 7,5% potential recovery would be possible. If two counter current rinse tanks were used then at a rinse ratio of 10 the potential chemical recovery would be 99%.

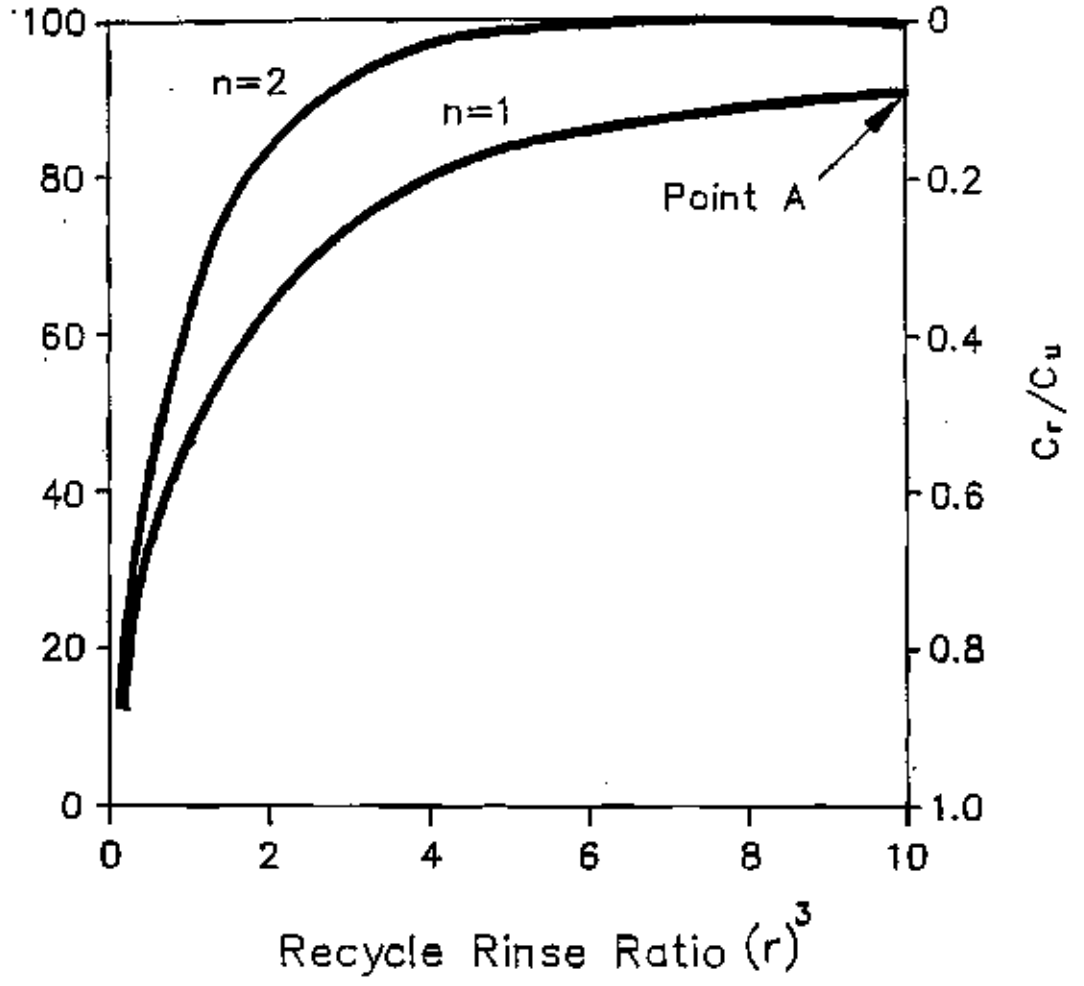
If the product quality (concentration of plating chemicals adhering on the work piece) is fixed then the relation between rinse ratio and number of rinse tanks is given by :-

$$\frac{C_p}{C_n} = r^n \qquad (3)$$

Assume a chrome plating tank operating at 300 g/l and a final rinse concentration of 15 mg/l, (C_p/C_n) would be 20 000. The effect of increasing the number of counter current rinse baths on the rinse ratio required to meet the required product specification is given in Table 3.3.

TABLE 3.3 The Effect of the Number of Rinse Tanks on the Rinse Water Requirements

Rinse Tanks	Rinse Ratios
1	20 000
2	141
3	27
4	12
5	7



^{3}r = recycle rinse (gal/h) − drag−out (gal/h).

Note: − r (recycle rinse flow) = surface evaporation from bath.

n = number of counterflow rinse tanks in recovery use.

Figure 3.3 : Percent Drag-Out Recovery with Rinse-and-Recycle System

The total mass flow of pollutants requiring treatment would remain constant, however, the volume of effluent requiring treatment would be greatly reduced as the number of rinse tanks increases. The physical size of the effluent treatment equipment could be decreased and the cost of pH adjustment chemicals would be reduced.

The mass flow of pollutants from a relatively valuable plating solution can be decreased by drag-out recovery system. The use of drag-out tanks usually results in less water savings than if that tank were used in either series or counter-current rinsing, however the mass of pollutant discharged is decreased. The hotter the plating bath (i.e. the greater the evaporation rate) the more attractive drag-out recovery becomes. A total of fifteen different rinsing configurations (Figure 3.4) have been evaluated by the US EPA (18) for water usage and effluent loadings. The results of the analysis of Watts Nickel system are reproduced in Table 3.4. The following conclusions were drawn from the above analysis.

(i) Single overflow rinses require extremely high flow rates to meet good rinsing criteria even at low drag-out rates.

(ii) Multiple rinse tanks can produce significant cost savings.

(iii) With low recycle ratios (1,37 or less) drag-out recovery is impractical because of high water requirements, unless three or more drag-out tanks are used or series rinsing follows drag-out.

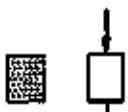
(iv) With recycle ratios of 2,75 or greater all additional tanks should be used as drag-out tanks rather than in parallel or series arrangements.

(v) Drag-in/drag-out systems usually must include series rinsing. The series systems become cost effective at recycle rates or below 1,25.

(vi) Plating baths that operate at lower temperatures have lower evaporation rates and offer fewer opportunities for rinsing recovery.

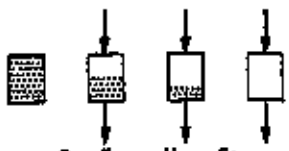
(vii) When the evaporation rate in the plating bath is low the most cost effect solution may be the concentration of the drag-out rinse itself, such as by evaporation, ion exchange, reverse osmosis etc before replacement in the plating tank.

ONE RINSE TANK

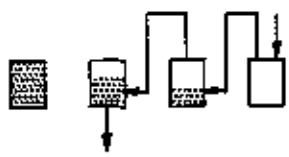


Configuration 1:
Single overflow

THREE RINSE TANKS

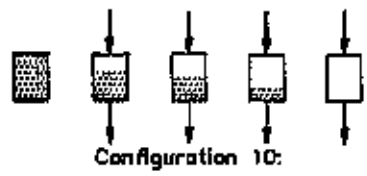


Configuration 5:
Three-stage parallel

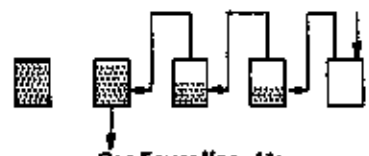


Configuration 6:
Three-stage series

FOUR RINSE TANKS

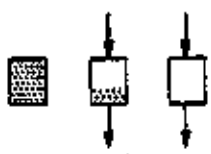


Configuration 10:
Four-stage parallel

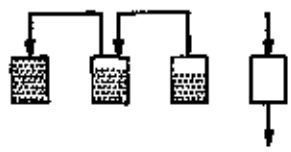


Configuration 11:
Four-stage series

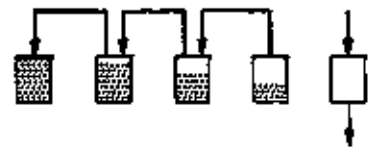
TWO RINSE TANKS



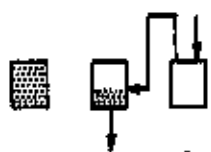
Configuration 2:
Two-stage parallel



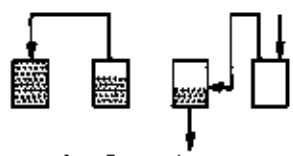
Configuration 7:
Two drag-out, one overflow



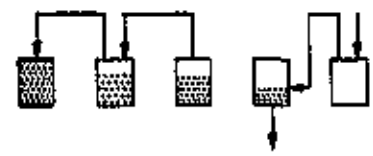
Configuration 12:
Three drag-out, one overflow



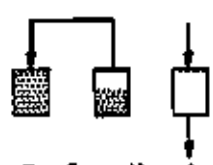
Configuration 3:
Two-stage series



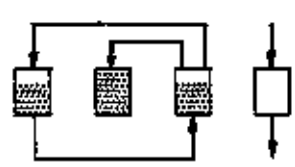
Configuration 8:
One drag-out, two-stage series



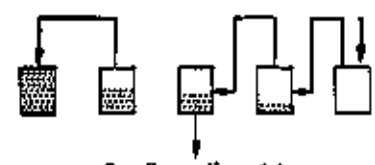
Configuration 13:
Two drag-out, two-stage series



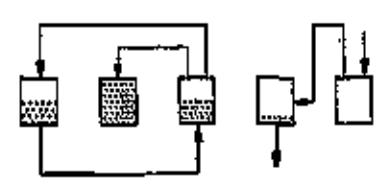
Configuration 4:
One drag-out, one overflow



Configuration 9:
Drag-in/drag-out, one overflow



Configuration 14:
One drag-out, three-stage series



Configuration 15:
Drag-in/drag-out, two-stage series

Note.—Decreasing heights of shading show that metals concentrations decrease.

Figure 3.4 : Rinsing Configuration

TABLE 3.4 Evaluation of Watts Nickel Plating System

Configuration	Water Usage gal/h	Plating Chemicals Lost lb/yr	Total Cost $/year
1	28,9	2 950	38 598
2	1,4	2 950	23 668
3	0,7	2 950	23 284
4	6,4	650	9 819
5	0,6	2 950	23 469
6	0,2	2 950	23 248
7	2,0	177	4 024
8	0,4	650	6 773
9	6,2	649	9 989
10	0,4	2 950	23 598
11	0,1	2 950	23 432
12	0,9	91	2 995
13	0,3	177	3 325
14	0,2	650	6 903
15	0,3	649	6 958

Parameter for the above analysis :

Plating bath concentration	85 g/l
Operating Temperature	60°C
Surface Area of Plating bath	2,5 m²
Max. conc. in final rinse	50 mg/l
Cost of water and sewage ($/1 000 US gal)	$2,00
Cost of a rinse tank ($/year)	240
Cost of treatment chemicals ($/lb Ni)	0,18
($/1 000 gal effluent)	0,21
Cost of sludge disposal ($/lb Ni)	1,15
Plating chemicals ($/lb Ni)	6,35
Deionised Water ($/year)	1 080

(All costs are 1981 US dollars)

The factors that influence the rate of drag-out include :-

(i) the velocity at which the work pieces are withdrawn from the plating tanks.
(ii) the geometry of the work pieces.
(iii) the positioning of the work pieces on the rack.
(iv) the drainage time allowed over the tank.
(v) the viscosity and density of the process solutions.
(vi) the temperature of the solution.

Adherance to the following points will reduce drag-out to a minimum :-

(i) the use of the minimum concentration of all plating chemicals that will enable the proper operations of the plating bath.
(ii) the operation of the bath at as a high a temperatures as is possible.
(iii) if there is a choice of two chemicals use the one with the greatest density and lowest surface tension.
(iv) the use of wetting agents.
(v) long time intervals are more profitably spent on a slow withdrawal from a plating bath rather than on a long draining period.
(vi) the racking objects such as to minimise drag-out.

3.1.2 Cyanide Removal

All effluent streams containing cyanide pass to the cyanide oxidation plant. The usual oxidation process is achieved by alkaline chlorination

$$2NaCN + 5Cl_2 + 12NaOH = 2Na_2CO_3 + 10NaCl + N_2 + 6H_2O$$

The chlorine can be supplied as a gas or as a sodium hypochlorite solution, small installations would utilise sodium hypochlorite solutions which while being more expensive than chlorine gas is more convenient to use. The high capital cost

of a chlorine gas installation is offset by low running costs in larger plants.

3.1.3 Hexavalent Chrome Removal

Hexavalent chrome (Cr(6))is far more toxic and difficult to remove by conventional precipitation than trivalent chrome hence all streams containing hexavalent chrome are reduced to trivalent chrome prior to subsequent treatment in the precipitation plant.

The reduction of hexavalent chrome is carried out in acid solutions with a variety of chemicals.

(a) Sulphur dioxide gas

$$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3$$

(b) Sodium metabisulphite and sulphuric acid

$$2CrO_3 + 3Na_2S_2O_5 + 3H_2O = 3Na_2SO_4 + 2Cr_2(SO_4)_3 + 3H_2O$$

(c) Sodium bisulphite and sulphuric acid

$$4CrO_3 + 6NaHSO_3 + 3H_2SO_4 = 3Na_2SO_4 + 2CrO_2(SO_4)_3 + 6H_2O$$

(d) Sodium sulphite and sulphuric acid

$$2CrO_3 + 3Na_2SO_3 + 3H_2SO_4 = 3Na_2SO_4 + Cr_2(SO_4)_3 + 3H_2O$$

(e) Ferrous sulphate and sulphuric acid

$$2CrO_3+6FeSO_47H_2O+6H_2SO_4 = 3Fe_2(SO_4)_3+Cr_2(SO_4)_3+48H_2O$$

The chemical cost of the last process is approximately double that of the other four (19).

The hexavalent chrome can be reduced in an alkaline medium (at a high cost) by using

(f) sodium hydrosulphite and sodium hydroxide.

$$Cr_2O_3 + 3Na_2S_2O_4 + 6NaOH = 6Na_2SO_3 + 2Cr(OH)_3$$

The chemical cost of the above process is about 4 times that of the processes (a) to (d).

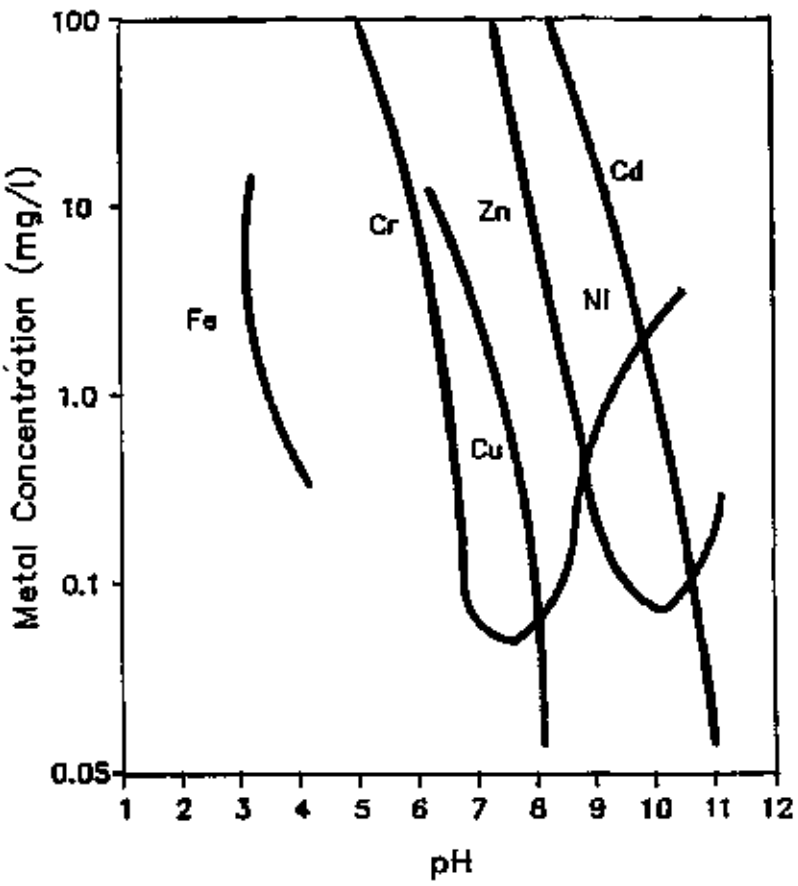
3.1.4 Heavy Metal Precipitation

Metal salts from simple inorganic compounds will tend to become insoluble in the neutral pH range, but not all metals will precipitate on neutralization and not all metals will precipitate at the same pH point and to the same extent. In view of the low discharge limits with regard to soluble metal content of a metal-finishing effluent, the initial problem is the selection of the optimum pH for precipitation. Some of metals are amphoteric, and therefore are soluble at alkaline pH values; examples of such metals are aluminium and zinc. Other metals require a relatively high pH to reach minimum solubility; this category would include nickel and copper.

With mixed waste streams, the best pH for the most complete separation will be that which limits the content of the most toxic of the metal salts and for which the regulatory limits are the most stringent. To meet regulatory requirements, it may be necessary to segregate streams to allow the best pH conditions for the particular metals to be precipitated. As a general rule, pH 8.0-8.5 is better (although not truly neutral) than is a pH closer to 7.00. Figure 3.5 shows some typical examples of the pH conditions at which the particular metals will be found at minimum concentration (9).

The presence of other dissolved salts affect the solubility of the metal hydroxides. Table 3.5 lists the metal content at various pH values if the precipitation occurs in either distilled water or hard water. Some of the metals may form more insoluble compounds when precipitated as carbonates rather than as the hydroxides. Chelating agents, organic acid salts, and the various wetting agents sometimes encountered in a mixed

rinse-water stream may make the quantitative precipitation of the various metals impossible.



SOURCE: U.S. Environmental Protection Agency, Waste Treatment: Upgrading Metal-Finishing Facilities To Reduce Pollution, EPA 625/3-73-002, July 1973.

Figure 3.5 : Precipitation of Metal Salts Versus pH

TABLE 3.5 Metal Residue after Precipitation in Distilled and Hard Water (20)

Precipitation												
pH	Fe^3		Ni		Cr^3		Zn		Cd		Cu^2	
	Distilled mg/l	Hard mg/l	Distilled mg/l	Hard mg/l	Distilled mg/l	Hard mg/l	Distilled mg/l	Hard mg/l	Distilled mg/l	Hard mg/l	Distilled mg/l	Hard mg/l
6,5	0	0,8	18	19,2	18	17,8	19	18,5	19	19,2	8	11
7,0	0	,4	16,5	18,9	15	13,7	18	17,8	18,5	18,4	1,3	5,8
8,0	0	0	12,5	10,8	5,3	7,1	1,3	9,1	15	15,2	,5	2,4
8,5	0	0	3,5	2,3	1,5	5	0	1,6	3,5	4,8	,2	1,7
9,0	0	0	2	,6	,4	3,4	1,5	1,5	,7	,9	0	1,2
10,0	0	0	0	0	0	,3	19,5	8,4	,3	0	0	,4

3.1.5 Centralised Waste Treatment System

The United State EPA has conducted a study on treating metal finishing effluents in centralised facilities (21). These centralised treatment schemes may assume various forms. One alternative is regionalised central treatment, in which all platers economically capable of shipping their waste use a facility designed to serve their region. Another alternative, group treatment, involves a facility owned and operated by a relatively small number of platers in close proximity. In the "plating city" centralised concept several platers may move into new facilities incorporating equipment for joint treatment of waste water. Various methods are available to individual plating shops for interacting with a centralised treatment facility.

Although many factors effect the economics, generalised studies show that substantial savings can be attained when more than 10 facilities are combined.

Previous studies of group treatment have shown that intercompany and other institutional barriers have interfered with firms reaching a mutually satisfactory joint arrangement. Questions related to allocating basic waste loads, allocating costs and appropriate siting, interfered with the implementation of these plans. However new US government financing alternatives and the increased likelihood of significant pretreatment requirements combined with toxic sludge discharge regulations have all increased the incentives for this system.

The projected investment required with and without group treatment for the 10 firms were given as follows (1980 US $)

		$
In-plant investment without group treatment		1 229 864
In-plant investment with group treatment	215 673	
Capital cost of group treatment plant	287 991	
		503 664
Capital Saving		726 200

The capital cost of the group treatment facility was broken down as follows:

	$
Chemical Oxidation	23 059
Physico-chemical treatment	72 496
Sludge dewatering	42 772
Storage	36 066
Laboratory, shelter, etc.	113 598
Total	$287 991

3.2 Specialised Methods

3.2.1 Cementation

Cementation (22) is the displacement of a metal from solution by a metal higher in the electromotive series, the definition can be expanded to cover reduction of any ionic species by contact with a metal of higher oxidation potential whether the reduced species is precipitated or not.

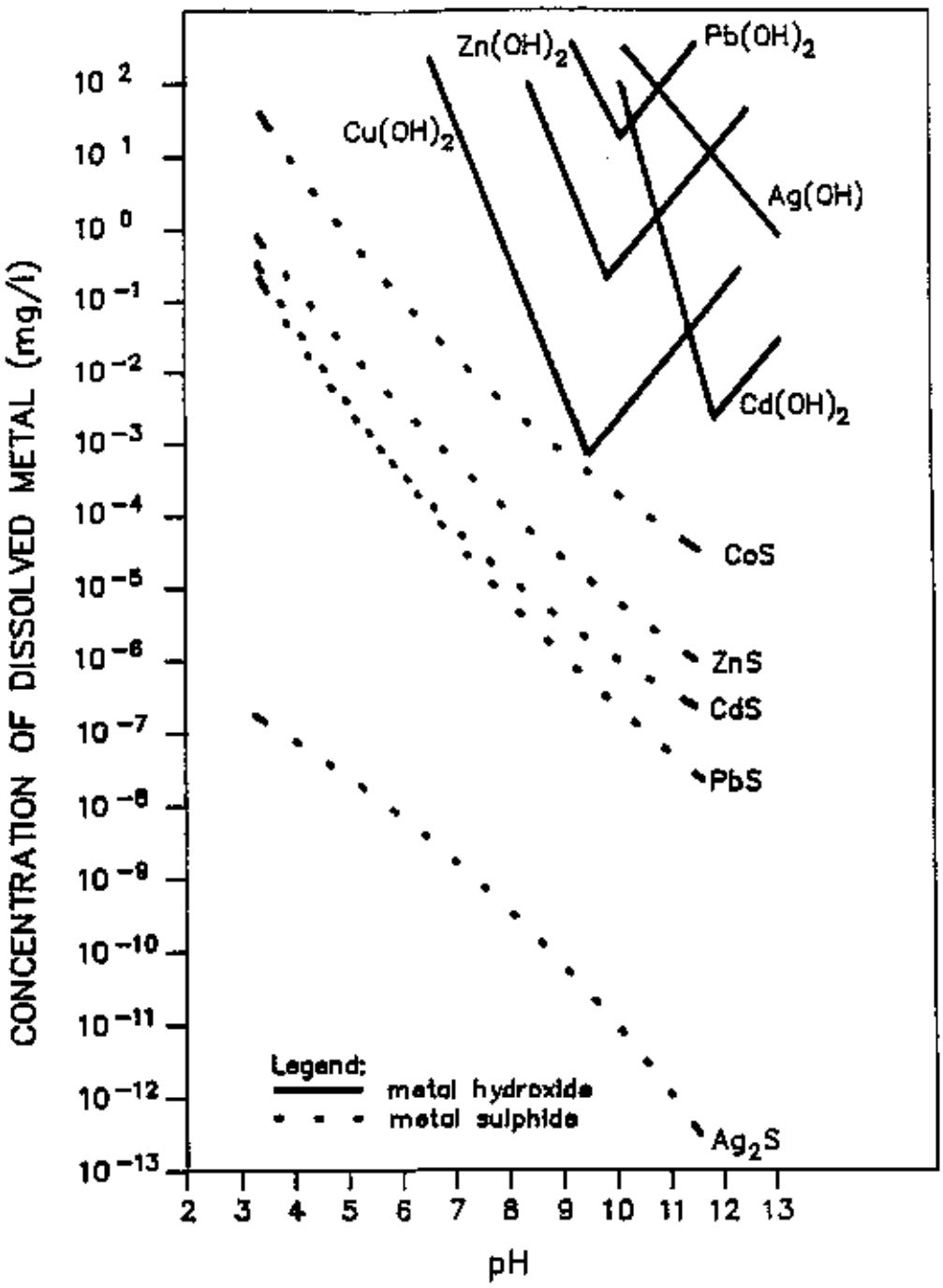
It can be used for precipitating silver from photographic processing solutions, the precipitation of copper from printed circuit etching solutions, the reduction of hexavalent chrome in waste streams from chrome plating, iriditing and chrome-inhibited cooling water blow-down. Zinc, aluminium and other metals having relatively high oxidation potentials may be utilised as reactants in place of iron. Alloys of certain alkaline earth metals (calcium, magnesium and barium) have been used (23).

Batch reactors using iron shot and feed solutions of 100 mg/l copper or 100 mg/l Cr(6) at a loading of 450 g copper or Cr(6) per m2 area of iron reduced the concentration of Cu and Cr(6) by 99% in less than 10 minutes

Continuous reactors with a residence time of 20 minutes achieved a 99% reduction in both copper and hexavalent chrome for feed solutions containing 100 mg/l of copper or hexavalent chrome (24).

3.2.2 Sulphide Precipitation

Sulphide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation (25) for removing various heavy metals from industrial waste waters. The high reactivity of sulphides with heavy metal ions and the insolubility of the heavy metal sulphides over a broad pH range are attractive features compared with the hydroxide precipitation process Figure 3.6. Sulphide precipitation can also achieve low metal solubilities in



Note.—Plotted data for metal sulphides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modern Alkaline Cooling Water Treatment," in Industrial Water Engineering (p. 31). Jan.—Feb. 1973.

Figure 3.6 : *Solubilities of Metal Hydroxides and Sulphides as a Function of pH*

the presence of certain complexing and chelating agents. There are two methods of adding the sulphide to the waste water.

(a) soluble sulphide precipitation (SSP)
(b) slightly soluble sulphide precipitation (SSSP)

In the soluble sulphide precipitation process the sulphide is added to the waste water in the form of a water soluble sulphide reagent such as sodium sulphide (Na_2S) or sodium hydrosulphide (NaHS). Operational problems with this process in controlling reagent demand so as to prevent overdose and the associated odour problem have been overcome by the use of a sulphide ion selective electrode to control the addition of the soluble sulphide. In addition the formulation of polyelectrolyte conditioners that effectively flocculate the fine metal sulphide particles has eliminated the difficulty in separating the precipitants from the discharge and has resulted in sludges that are easily dewatered.

The slightly soluble sulphide precipitation process uses a freshly prepared ferrous sulphide solution (prepared by reacting $FeSO_4$ and NaHS) as the source of sulphide ions needed to precipitate the metals from the wastewater. The process operates on the principle that FeS will dissociate into ferrous ions and sulphide ions to the degree predicted by its solubility product. As sulphide ions are consumed, additional FeS will dissociate to maintain the equilibrium concentration of sulphide ions. In alkaline solutions the ferrous ions will precipitate as ferrous hydroxide. Because most heavy metals have sulphides less soluble than ferrous sulphide, they will precipitate as metal sulphides.

An advantages of the SSSP is the absence of any detectable hydrogen sulphide odour. Secondly, the SSSP will reduce hexavalent chrome to the trivalent state under the same conditions required for metal precipitation thus eliminating the need to segregate and pretreat chrome waste streams.

Disadvantages of SSSP is that the process requires considerably greater than stoichiometric reagent consumption and produces a significantly greater volume of sludge than either the hydroxide or SSP processes.

Figure 3.7 compares typical process flow diagrams of a hydroxide treatment system and both types of sulphide systems. Most of the elements of the sulphide system are common to the hydroxide precipitation treatment process. The sulphide treatment process also can be used as a polishing system after a conventional hydroxide precipitation/clarification process to significantly reduce the consumption of sulphide reagent.

The final disposal of the sludge is an open question in that although the metal ion leachability is lower for sulphides than hydroxides the long term effects of weathering and bacterial and air oxidation of sulphide sludges has not been evaluated.

The potential hazard of sulphides coming in contact with acids with the evolution of toxic H_2S fumes emphasises the need to control a low sulphide residual in the discharge.

3.2.3 Lancy Integrated System

The integrated system (26, 27) consists of a recirculated chemical treatment wash solution integrated into the metal fnishing process line. Parts being removed from a toxic process solution are rinsed in this treatment wash solution before being rinsed in water (Figure 3.8). This approach greatly reduces the input of dissolved salts to the rinse water (compared to conventional rinsing) hence far less water is required to accomplish satisfactory rinsing and reductions in rinse water usage of up to

80% can be achieved. As the toxic dragout solutions are not diluted and the neutralisation takes place in the presence of a high excess of treatment chemicals the resulting precipitates are more dense and settle faster compared to the usual method of settling similar precipitates from dilute rinse water.

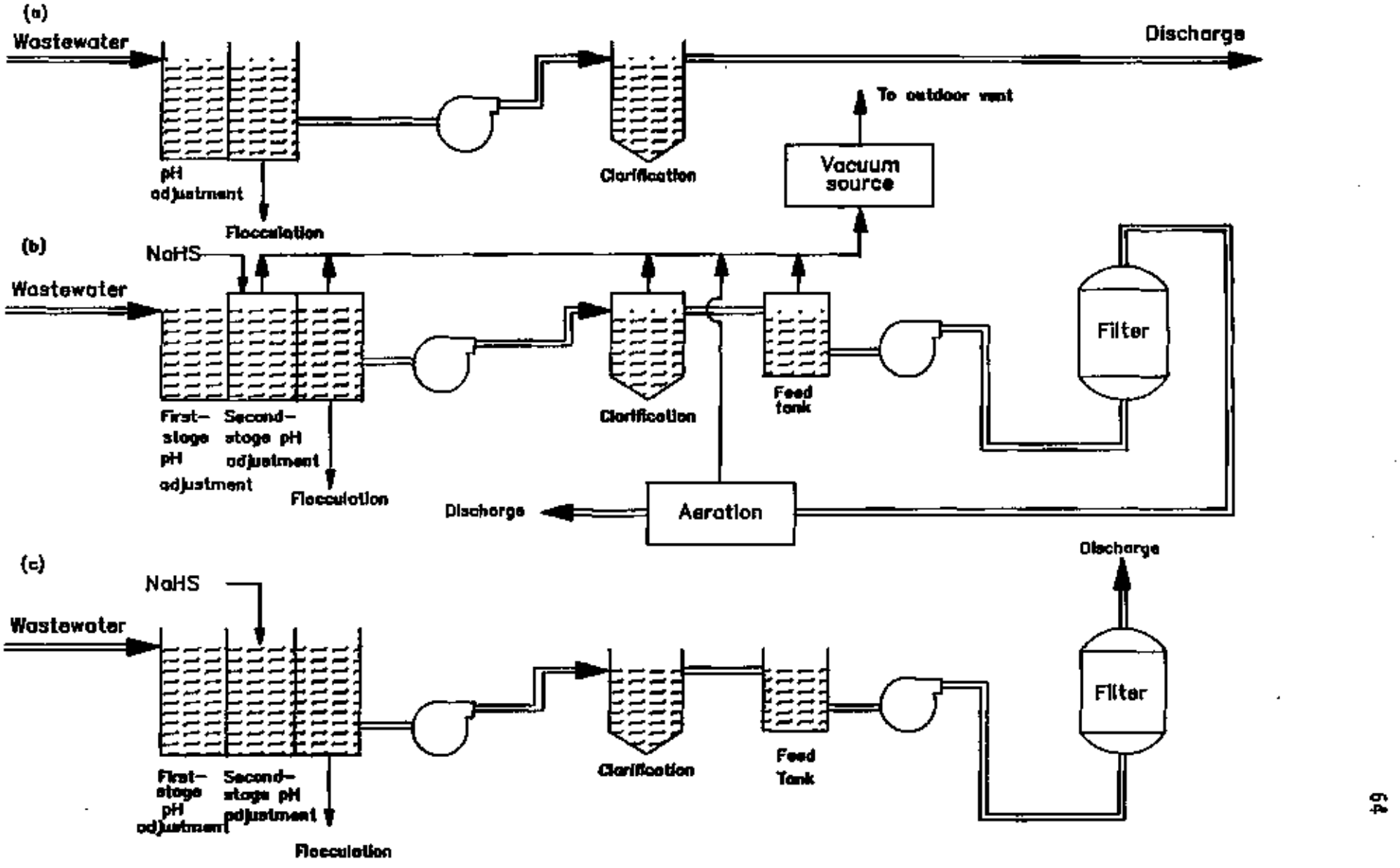


Figure 3.7 : *Conversion of Hydroxide Treatment System to Use SSP: (a) Hydroxide Precipitation System, (b) SSP System, and (c) SSP System with Automatic Control of Sulphide Residual*

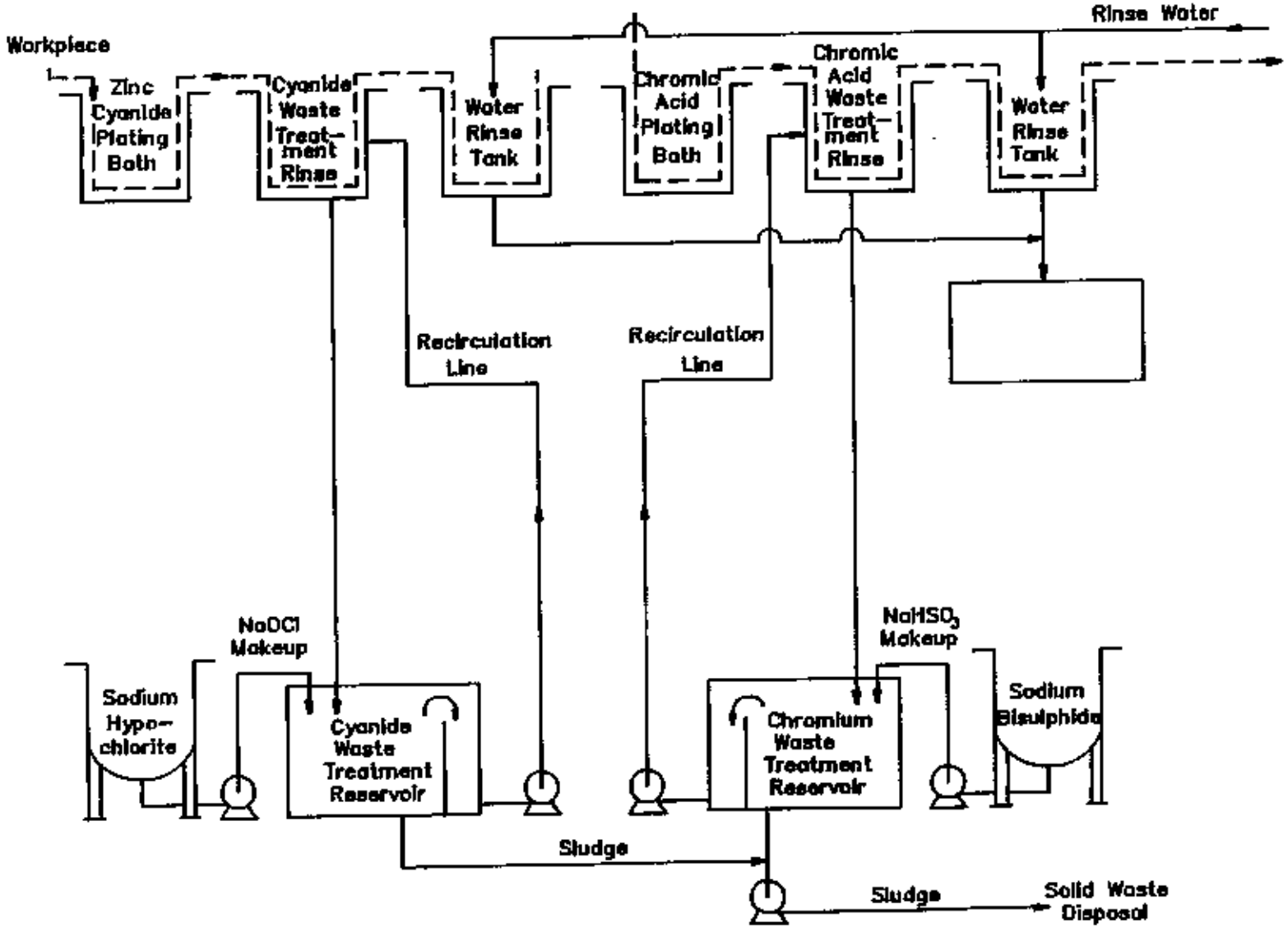


Figure 3.8 : Integrated Treatment for Chromium and Cyanide Plating Rinse Water

The treatment wash solutions must be chemically formulated to suit the particular contaminant for which it is intended and separate closed loop systems must be provided for each type of contaminant. The following types of contaminants can be treated :

(i) Cyanide compounds such as sodium and potassim cyanide and also their metal complexes with zinc, cadmium, copper, silver and gold.

(ii) Chromic acid wastes containing high concentrations of chromic acid.

(iii) Chromate compounds containing low concentrations of chromate chemicals.

(iv) Nickel from sulphate and chloride based solutions.

(v) Copper from acid solutions such as sulphuric/nitric bright dips, acid copper plating solutions, and chelated copper complex plating solutions as used in the plating of plastics.

The chemistry of these systems is as follows:

Cyanide

$$2NaCN + 8NaOH + 5Cl_2 = 10NaCl + 2CO_2 + N_2 + 4H_2O$$

Chromium I

$$2H_2CrO_4 + 3SO_2 = Cr_2(SO_4)_3 + 2H_2O$$

Chromium II

$$Cr_2(SO_4)_3 + 3Na_2CO_3 + 2H_2O = Cr_2(OH)_4CO_3 + 3Na_2SO_4 + 2CO_2$$

and

$$2Na_2CrO_4 + 3Na_2S_2O_4 + Na_2CO_3 + 2H_2O = Cr_2(OH)_4CO_3 + 6Na_2SO_4$$

Nickel

$$2NiSO_4 + 2NaOH + Na_2CO_3 = Ni_2(OH)_2CO_3 + Na_2SO_4$$

Copper

$$CuSO_4 + H_2SO_4 + Na_2S_2O_4 + 8NaOH = Cu_2O + 2Na_2SO_3 + 3Na_2{}_4 + 5H_2O$$

The Chrome II treatment solution contains both reducing and neutralising chemicals. It is used as a single step treatment wash after low concentration chromate dips. The Chrome I treatment solution is operated at a low pH range and can thus use a much less expensive reducing agent than can the Chrome II system. Following highly concentrated chrome processing solutions, the Chrome I treatment wash is used first to accomplish reduction of the hexavalent chrome solution economically. The Chrome II wash, which follows, then neutralises the acidic Chrome I film and precipitates the trivalent chrome as the basic carbonate. The system is summarised in Table 3.6.

TABLE 3.6 Summary of Integrated Treatment Systems

System	Process Treated	Treatment Chemicals and Concentration	Metals Precipitated
Cyanide	Zinc, Cadmium Copper, Silver and Gold plating	Chlorine gas 800 - 2 500 mg/l Caustic Soda pH 11 - 12,8	Zinc Cadmium Copper Gold
Chrome I	Chromium plating Etching of Plastics	Sulphur dioxide gas 1 000 - 2 500 mg/l	
Chrome II	Chromium plating chromate dipping of Zinc, Cadmium and aluminium ; Etching of Plastics ; Chromic acid anodising	Sodium Hydrosulphite 200 - 500 mg/l Sodium Carbonate pH 7,5 - 8,5	Chromium Zinc Cadmium Aluminium
Nickel	Nickel plating	Sodium Carbonate pH 8,5 - 9,5 Sodium Hydroxide	Nickel
Copper	Acid copper plating Copper and Brass bright dipping	Sodium Hydrosulphite 500 - 700 mg/l Caustic Soda pH 8,5 - 9,5	Copper Zinc

The total dissolved solids concentration in the integrated treatment solutions (typically 75-120 g/l) is much lower than in the preceding process baths (typically 250-400 g/l) and the volume of the solution film carried on a given work piece is the same when it emerges from either solution. The TDS of the effluent from a plating shop which incorporates an Integrated System is lower than the TDS in the effluent from a similar shop which treats its effluent in the conventional manner. This is because the volume of effluent treated in the latter case is much larger than in the Integrated System and although both systems require an excess of reagents (acids, bases, precipitants etc) the larger volumes which are associated with the conventional treatement plant results in a greater mass of reagent addition. The actual TDS load from the Integrated System is about 25% of that from a conventional system.

Modifications to the process include adding harmless cations such as calcium and magnesium to preferential displace cadmium or copper from certain chelating containing rinses and the substitution of the more stable hydrazine hydrate in place of sodium hydrosulfite as the reducing agent.

The average effluent analysis over a year following the implementation of the Integrated system is given in Table 3.7.

TABLE 3.7 Average Effluent Analysis after Treatment by the Integrated System

pH	7,8
CN	0,03
Cr (iv)	0,02
Cr (iii)	0,01
Cu	0,09
Ni	0,21
Zn	1,12
Cd	0,25

All values, except pH, in mg/l

3.2.4 Ozone Treatment

Ozone can be used as an alternative to chlorine in the oxidation of cyanide (28). The cyanide ion is oxidised to cyanate which is then hydrolysed to carbon dioxide and ammonia.

$$CN^- + O_3 = CNO^- + O_2$$

$$CNO^- + 2H_2O = CO_2 + NH_3 + OH^-$$

The use of ozone has been hampered by both the equipment used for treatment and the nature of ozone itself. The advantages of ozone over chlorine are :-

(i) no reagent storage necessary
(ii) operation at ambient temperature
(iii) process is well suited to automation.

A case study has been presented (28) in which mixed effluent from a bumper refurbishing and recycling plating shop was treated by ozone and rotary vacuum filtration. The effluent contained nickel, chrome, copper, cyanide and iron. The hexavalent chrome was reduced to trivalent chrome with sodium bisulfite and the pH was increased to 10,5 to 11,5 by lime addition. The effluent containing suspended metal hydroxides and cyanide was then contacted with ozone in a spinning bowl reactor. The high speed of the bowl (40 000 rpm) atomised the effluent increasing the contact surface area between the effluent and the ozone. The suspended solids were removed on a rotary vacuum filter. The high solids content of the sludge (75%) was due to the formation of metal oxides which had a lower degree of hydration compared to the corresponding metal hydroxide. The effluent on which the system was evaluated was very dilute and data on more concentrated effluent was unobtainable. A summary of operating results are presented in Table 3.8.

Table 3,8 Effluent Treatment using Lime and Ozone

	Influent	Effluent	% Removal
Cyanide	1,02	0,08	92
Total Chrome	1,41	0,40	72
Copper	9,45	0,05	99
Nickel	20,32	0,13	99
TSS	135	11,6	91
pH	6,4	8,4	

All concentrations except pH in mg/l.

The capital costs (1980) of a 5,85 m^3/h and 23,4 m^3/h plant were given as $200 000 and $250 000 (4 800 hours/year operation). The operating costs were calculated to be $56 650 and $89 190 per year or $2,02 and $0,79 per m^3 respectively.

3,3 Evaporation

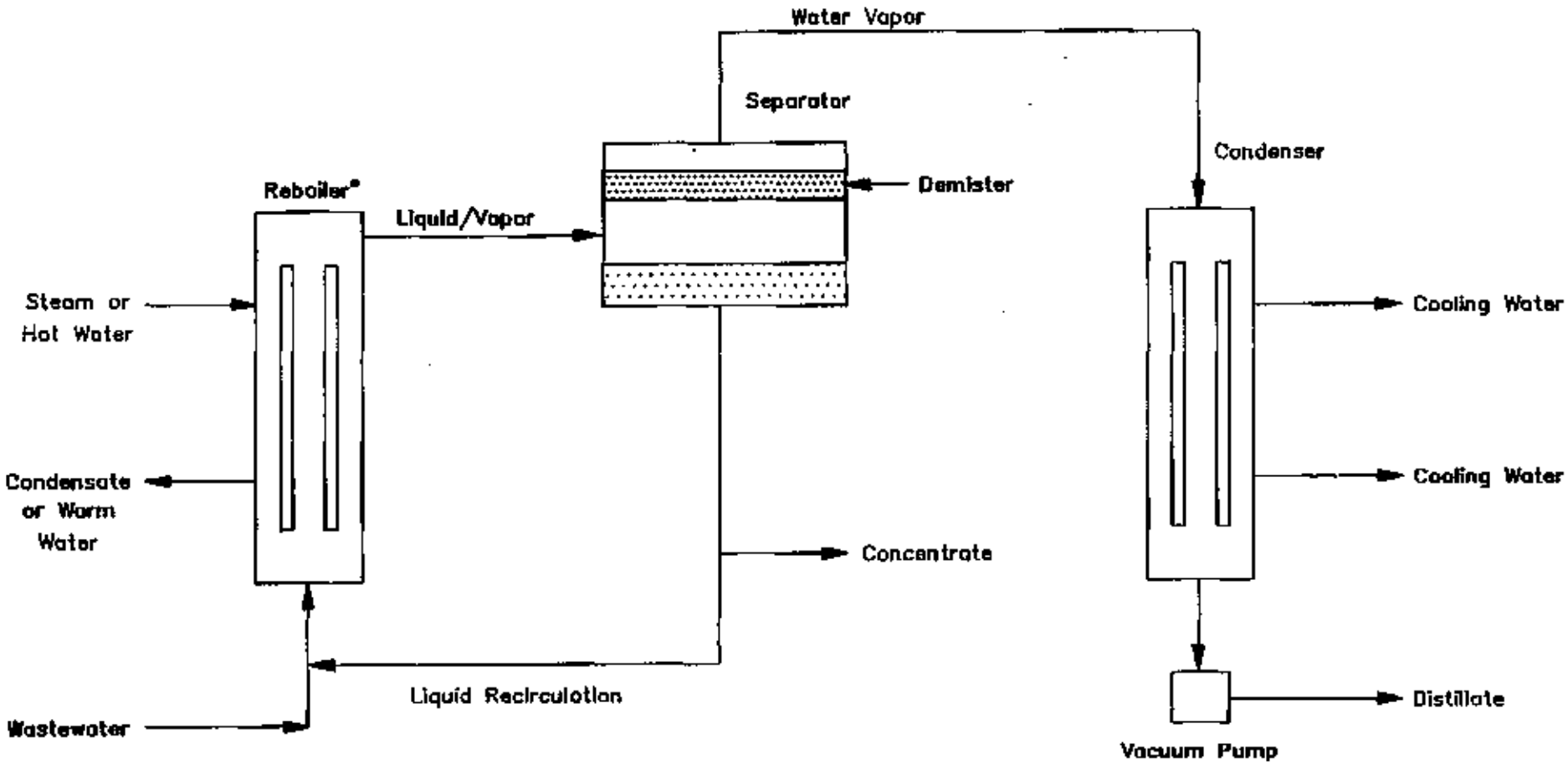
Evaporation achieves recovery by distilling waste water until there is a sufficient concentration of plating chemicals to allow reuse in the plating operation. Because of the thermal energy costs of the operation, evaporators are not usually considered for recovery of plating chemicals from diluted waste waters. Reverse osmosis can be used to preconcentrate the rinse wter prior to evaporation. Four types of evaporators are used by the electroplating industry (29):-

(a) rising film evaporators
(b) flash evaporators using waste heat
(c) submerged tube evaporators
(d) atmospheric evaporators

Site specific conditions and the mode of operation influence the selection of one system over another. The steam requirements can be significantly reduced by installing multiple effect evaporators or by using mechanical recompression. Vacuum evaporators lower the boiling point of the solution and therefore decreases the rate of cyanide decomposition. It also reduced the amount of carbon dioxide absorption and air entrainment.

3.3.1 Rising Film Evaporators

Rising film evaporators consists of a reboiler, seperator and condensor. The reboiler is a shell-and-tube heat exchanger in which heat from low pressure steam or hot water is transfered to the wastewater Figure 3.9. Because plating chemicals are susceptible to degradation at high temperatures the evaporation is carried out under a vacuum such that the boiling temperature of 40° to 85°C is achieved. The fast rate at which heat is transferred to the thin film minimises crystalisation and precipitation on the heat exchange surfaces resulting in lower maintenance and higher heat transfer efficiency. The wastewater leaves the reboiler as a vapour droplet mixture which enters the separator which separates the two phases. The vapour is then condensed and removed from the system as distillate. The liquid phase is recirculated through the reboiler until the concentration of the plating solution reaches a preset level. The evaporator can operate in either a continuous or batch mode.



*The heating medium and wastewater may be interchanged in the shell and tubes, depending on the manufacturer.

Figure 3.9 : Rinsing Film Evaporation for Chemical Recovery

3.3.2 Flash Evaporators

Flash evaporators are of the same basic design as rising film evaporators. The main difference is that plating solution from the plating batch is recirculated continuously through the evaporator. During the plating operation the temperature of the plating bath increases because of the electrolytic process. As an alternative to the installation of cooling coils, the recirculation of the contents of the plating bath through the flash evaporator provides most of the energy required for evaporation of the wastewater and cools the plating bath solution as well. Because the quantity of heat provided by the flash cooling of the plating bath solution is small compared to the latent heat provided by steam heating, flash evaporation usually is limited to large, high temperature installations.

3.3.3 Submerged Tube Evaporator

Submerged tube evaporators operate on a slightly different principle from that of film or flash evaporators for supplying thermal energy to the wastewater. A single effect unit consists of one vessel that includes internal heating coils for evaporation, a moisture separator and cooling coils for condensing water vapour. Figure 3.10 The wastewater is not recirculated, unlike that of rising film and flash evaporators. The reduced operating pressure is created by diverting some of the cooling water through an eductor. The cost for submerged tube evaporators is lower than that for rising film or flash untis primarily because of the integrated evaporation/condensation single-unit design, although the thermal demand is the same as rising film units the cooling water requirement are greater.

3.3.4 Atmospheric Evaporation

Atmospheric evaporators Figure 3.11 do not recover distillate for reuse nor operate under a vacuum. Wastewater is evaporated by

allowing it to humidify air passing through a packed tower. The humidified air is exhausted to atmosphere eliminating the need for cooling water and a condenser. The concentrate from the reservoir is recirculated through the packed tower after passing through a heat exchange which raises the temperature to about 70°C. Because the exhaust air removes some of the heat supplied by the wastewater heat exchanger this type of unit requires approximately 20% more steam than do evaporators of other designs. Deionised water must be used in the rinse tanks to minimise scale deposits during evaporation.

The payback period for closed loop treatment of chromic acid plating dragout (7,57 l/h at 300 g/l and 5 000 hour/year) assuming a rinse water flow of 187 l/h was 4,9 years. If the evaporator was used to concentrate the static dragout tank only the payback would be 3,4 years and the untreated effluent flow would be 257 l/h at 750 mg/l chromic acid.

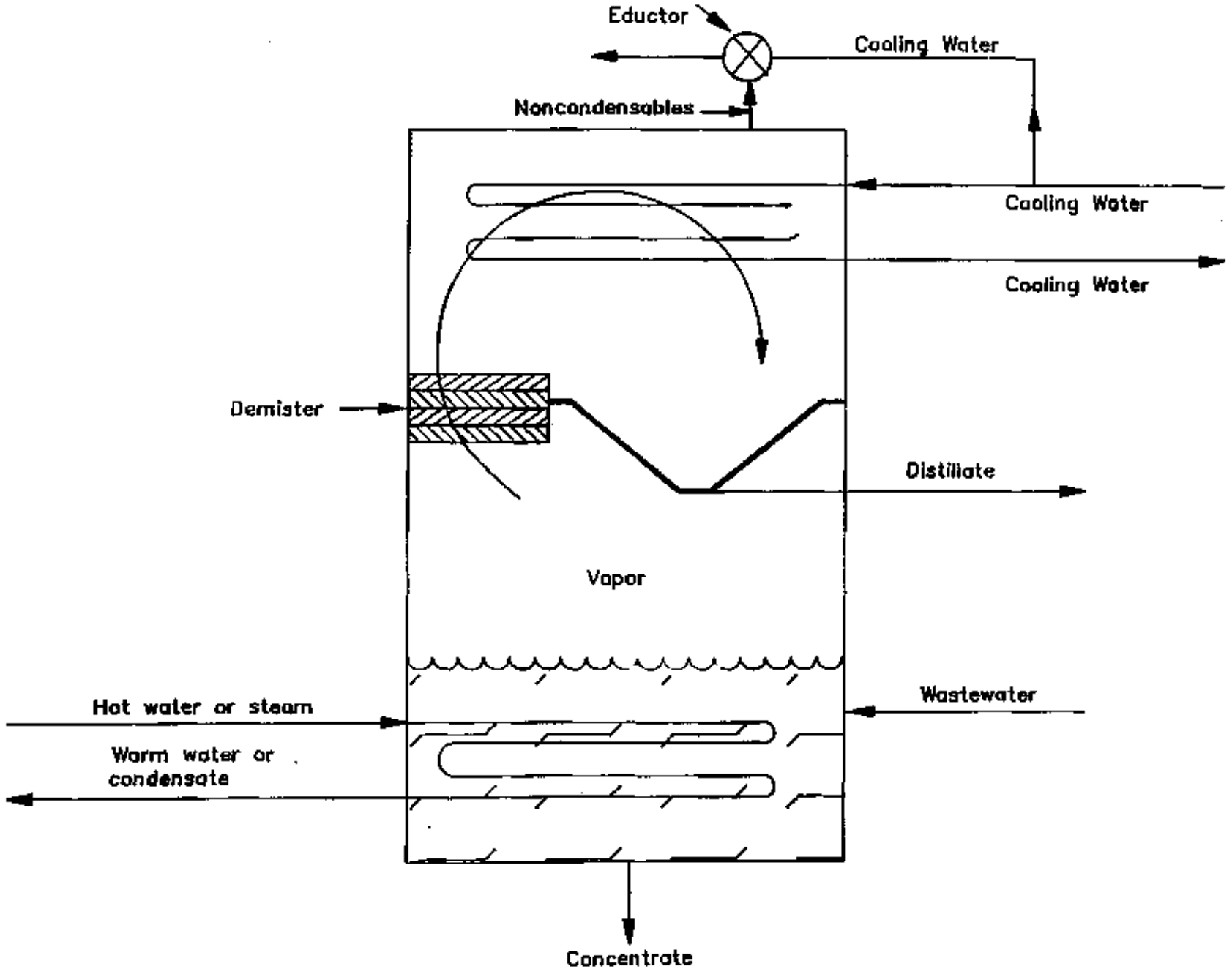


Figure 3.10 : Submerged Tube Evaporation for Chemical Recovery

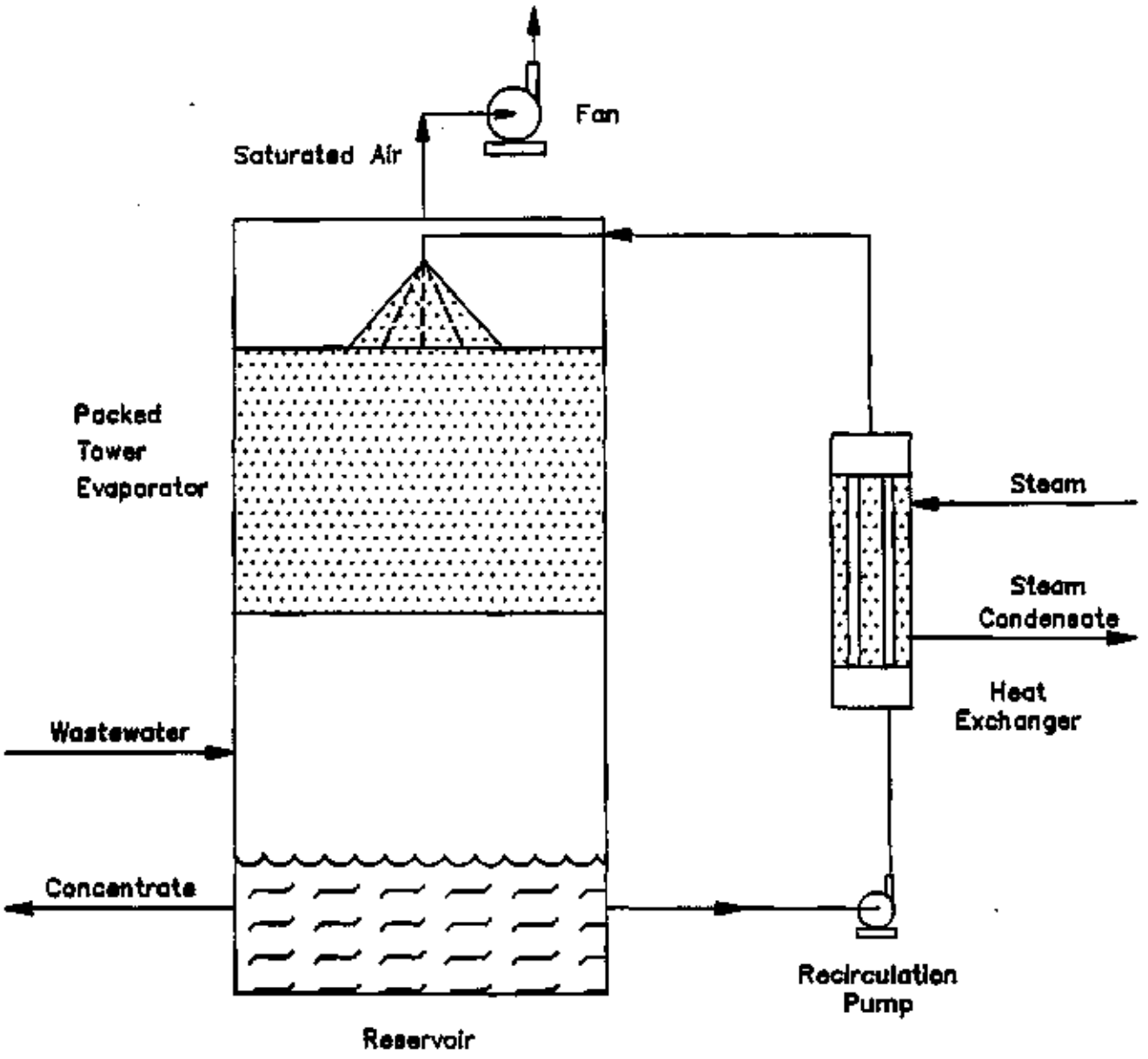


Figure 3.11 : *Atmospheric Evaporation for Chemical Recovery*

3.4 Membrane Processes

Membrane processes of commercial interest are :-

(a) Pressure-driven

(i) Hyperfiltration (HF) or Reverse Osmosis (RO) is used for the desalination of water i.e. the removal of salts. Two main types of membrane are available : those for brackish water (2-8 g/l TDS) and those for seawater (35 g/l TDS).

(ii) Ultrafiltration (UF) is used for the separation of a range of macromolecules (nominal molecular weight cut-offs of 1 000 up to 300 000). The operating pressures are below 1 MPa.

(iii) Cross-flow microfiltration (CFMF) for the separation of colloidal and large macromolecular solutions. These membranes pass smaller molecules and the solvent (aqueous) phase. Normally low pressures, below 1 MPa, are used.

(b) Electrically-Driven

(i) Electrodialysis (ED) uses ion exchange membranes for the transport of ions through the membrane under a dc electric field. Normally ED is used for brackish water desalination, but is also capable of concentrating highly saline solutions (200 g/l TDS).

(ii) Reversal Electrodialysis (EDR) uses changes in polarity and flow at periodic intervals so that salts are transferred in opposite directions across the membranes. This overcomes many scaling and fouling problems.

3.4.1 Reverse Osmosis

In reverse osmosis a pressurised saline solution is separated from the solutes and flows through an appropriate membrane. The permeate (product), which generally emerges at near atmospheric pressure, is reduced in salt content while the feed solution concommitantly increases in salt concentration. For brackish waters the operating pressure is generally 2,5 to 4,0 MPa and for seawater 5,5 to 6,5 MPa. These pressures are used to provide reasonable membrane flux rates and to overcome osmotic back pressure Figure 3.12. The flux equation is :-

$$J = k.A.(\Delta P - \Delta \pi)$$

where

J = membrane flux (eg l/m3h)
k = membrane permeability constant
A = membrane area
ΔP = applied pressure gradient
$\Delta \pi$ = osmotic pressure gradient.

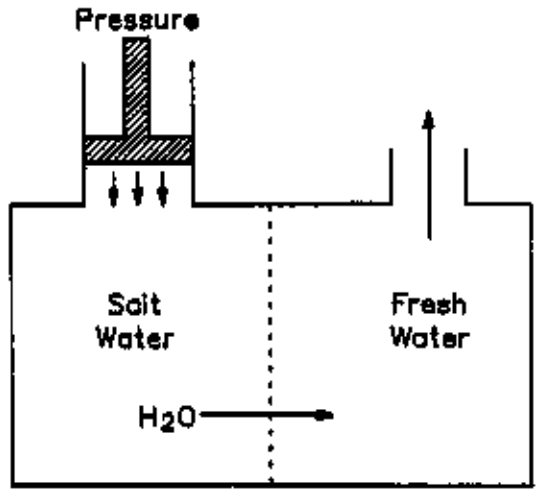
The elements of the process are shown in Figure 3.13. The cross-flow nature of the system produces two streams - permeate and brine or concentrate and prevents the build-up of the rejected species at the separation surface.

The following types of membranes are available:

(i) Cellulose Acetate

Normally cellulose di-acetate is used and an assymetric membrane with a dense skin is produced. This is the rejection surface and is usually 0,2-0,5 % of the total membrane thickness.

Available in spiral, hollow fine-fibre, plate and frame and tubular configurations. Although it has several limitations, it is still the most widely used membrane material.



The tendency of water to diffuse through a membrane into a salt solution (osmosis) can be reversed by applying a pressure greater than the osmotic pressure of a solution

Figure 3.12 : *Reverse Osmosis*

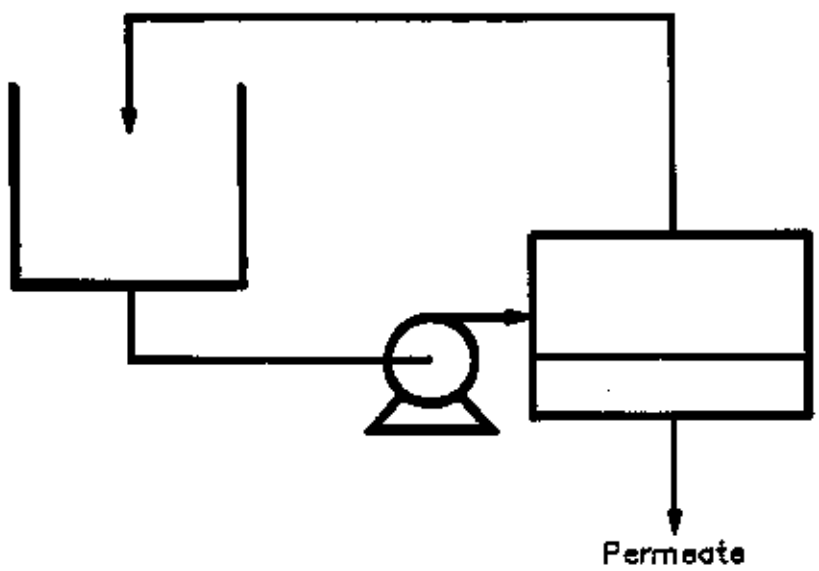


Figure 3.13 : *Reverse Osmosis Batch System*

Physical limits are a temperature of about 30°C and a pH range of 4-7, but the membrane has reasonable chlorine resistance. It is subject to compaction and microbial attack and does not have a high rejection for organic species, it can only be cleaned with mild chemical solutions.

(ii) Polyamide Hollow Fine-Fibre

This is used in the Dupont Permasep module and although the membrane has a low permeability, it has a very high packing density. The modules have similar production rates to spiral modules on both a cost and physical space basis.

Temperature limit is 40°C and the pH range is 4-10. The membrane has zero chlorine resistance.

(iii) Thin Film Composites (TFC)

This membrane technology was pioneered by UOP Fluid Systems in 1977 and consists of a porous support (usually polysulphone) onto which is laid a separate rejection layer by polymerisation. The UOP PA-300 membrane is only 0,00005 mm thick compared to the 0.05 mm of the base layer. This membrane has a temperature limit of 45°C and a pH range of 3-10. It has no chlorine resistance. Rejection of organics is relatively good.

Several other companies are now producing similar membranes :-

FilmTec FT30 (which claims chlorine resistance)
Teijin PBIL
Toray

(iv) Dynamic Membranes

These are formed in situ by solution chemistry on porous tubes (e.g. stainless steel). They have not been widely developed on a commercial basis and have been mainly used for industrial effluent applications. They may have potential for the treatment of highly fouling wastewaters as the membranes are easily replaced at low cost.

Reverse osmosis offers potential in the following metal finishing applications: reclamation of plating salts; treatment of total plant effluent; recovery of Cl specific solutes; production of pure water; and alkali cleaner recovery.

Plating salts in the rinse effluent can be concentrated by reverse osmosis and returned to the plating bath. The concentration at which the plating chemicals are recycled is limited by the osmotic pressure of the solution hence in practice RO has to be used in conjunction with evaporation. The natural evaporation from hot baths (e.g. Watts nickel) is sufficient and supplementary evaporation is not required.

Because RO membranes reject most organic brighteners along with the plating salts, RO cannot be used for dual nickel applications.

The capital cost (34) of an RO system for recovering nickel rinse water (2250 mg/l nickel salts) is $600 per cubic meter per day (1980 prices). Operating costs range from $0,20 to $0,54 per cubic meter of feed water.

The complete factory effluent can be treated by reverse osmosis. The salts and organic chemicals can be concentrated 20 fold and the permeate recycled to the rinse baths.

The volume of concentrate produced from the reverse osmosis plant would be about 5% of the feed volume and could be treated by hydroxide or sulphide precipitation. The filtered sludge would be suitable for disposal in an approved land fill site and the filtrate recycled to the reverse osmosis plant.

The advantages of reverse osmosis for the end of line treatment of plating effluents are:-

(i) both free and chelated metals are rejected and concentrated by the membrane,

(ii) the permeate could be reused in the plating process,

(iii) the amount of chemicals required for the hydroxide or sulphide precipitation of the concentrate would be reduced.

A series of experiments were conducted for the US EPA to evaluate the application of R.O. to plating chemical recovery (30, 31). These experiments examined the performance and life of membranes that were commercially available, as well as advanced membranes with promising applicability.

A summary of the tests using commercially available membranes (1976) is presented in Table 3.9. More recent tests carried out with the FilmTec FT 30 membrane on zinc and silver cyanide electro plating rinse water over a pH range of 8 to 12 indicate a cation rejection of 98 to 99%. Cyanide rejections at pH 11 to 12 were 92 to 95%. The advantage of the FT 30 membrane over the earlier membranes is its higher flux, wider pH tolerance, higher salt rejection and higher temperature stability. This membrane is susceptible to "poisoning" by nonionic and cationic detergents and class 2 nickel bath brighteners (32).

Table 3.9 Existing Demonstrated Commercial Application of R.O. in Metal Finishing Industry

Plating Bath Chemical	Membrane Type — Configuration	Application Operation Criteria	Operating Experience and Recommendations
Bright nickel	Cellulose acetate/ spiral wound	Closed-loop drag-out chemical recovery and purified rinse water recycle, feed water pretreatment consisting of pre-filtration with diatomaceous earth precoat filter and/or micron cartridge filters. Conductivity, flow rates, pressure are monitored; pH (5–6) not adjusted prior to feed. Surface evaporation make-up with demineralized water. Plant start-up November, 1977.	Membrane life was a minimum of 18 months. Although regularly back-flushed, there is a gradual fouling of membrane. Experienced corrosion inside carbon steel shell of pressure vessel. Should be stainless steel, plastic, or fiberglass.
Watts nickel	Cellulose acetate/ spiral wound	Closed-loop drag-out chemical recovery and purified rinse water recycle, feed water pretreatment consisting of pre-filtration with 10–15 μm cartridge filters, pH adjustment to 4.0, conductivity, flow rates, pressure are monitored, water to replace surface evaporation losses is supplied by separate RO unit. Plant start-up September, 1978.	No sign of membrane fouling so far. Normal operating time is 18–24 hrs/day. Cumulative operating time since start-up is 736 hours. Replace prefilters every 3–4 days. No problem of algae growth in rinse tanks.
Acid copper	Polyamide/ hollow fiber	Open-loop purification of rinse water overflow from several combined rinses and recycle of rinse water to plating operation, concentrate is further treated for metal precipitation with lime. Pretreatment of feed consisting of pre-filtration with 10 μm cartridge filter followed by sand filter and 5 μm cartridge filter. pH of feed adjusted to 3.0–3.5. Flow rate, conductivity and pressure are monitored.	Experiencing approximately 12–18 months membrane life. Using citrus acid buffered ammonium hydroxide to wash each stage once a week, further back flushing is done on each module every month. Average operating time is about 13 hours/day. Maximum temperature is 95°F.
Acid zinc	Polyamide/ hollow fiber	Same as above acid copper except pretreatment excludes pH adjustment to 8.0 and addition of Bactericide. Plant start-up approximately 1978.	Average operating time about 22 hrs/day.
Copper cyanide	Polyamide/ hollow fiber	Closed-loop drag-out chemical recovery and purified rinse water recycle, feed water pretreatment consisting of filtration with 10 μm bag-type filter plus 1.2 μm & 0.45 μm cartridge filters in series, no pH adjustment required (pH = 10.0–10.5), surface evaporation make-up with DI water. Plant start-up Approximately November, 1974.	Approximate membrane life is 5½ years. No back-flushing done at all. Replaces prefilters once per week on the average. Average operation 8 hrs/day, 5 days per week.
Bright nickel	Polyamide/ hollow fiber	Closed-loop drag-out chemical recovery and purified rinse water recycle, pretreatment is the same as copper cyanide unit above, no pH adjustment (pH = 7.0), surface evaporation make-up with DI water. Plant start-up March, 1975	Membrane life approximately 5 years. No back-flushing done. Replaces prefilters once per week. Average operation 8 hrs/day, 5 days/week.
Acid copper	Polyamide/ hollow fiber	Open-loop purification of mixed rinse water overflow and recycle of purified rinse water to plating operations, reject containing mixed metal salts is further concentrated in solar evaporation ponds. Pretreatment of feed water consisting of filtration with diatomaceous earth filter followed by 5 μm and 0.5 μm cartridge filters, ultraviolet sterilization and chemical pretreatment limits algae, pH adjustment prior to RO to 4.5–5.0. Flow rate, conductivity, pressure are monitored. Surface evaporation make-up is demineralized city water. Approximate start-up 1976.	Operation 11 hr/day maximum, bacteria and algae growth is a problem. Cleaning with formaldehyde is done daily to prevent fouling with bacteria or algae. Hypochlorite solution used every 2–3 months to control further algae growth.
Mixed waste heavy metals (Cu, Cr, etc.)	Cellulose acetate/ spiral-wound	Purification of mixed wastewater effluent from primary treatment system and recycle of rinse water to plating operation. Reject is further concentrated in solar evaporation ponds. Pretreatment of feed water consisting of filtration in gravity filters, vacuum DE filters and 5 μm cartridge filter, pH adjustment to 5–6 prior to RO feed. Designed for zero discharge to sewer. Plant start-up approximately March, 1977.	Membrane life approximately 3 years. Normal operation 16 hrs/day, 5 days/week, operation by one engineer per shift plus one laborer, no major problems.

A review of existing reverse osmosis installations (1983) has been compiled (34) and is reproduced below.

3.4.1.1 Nickel Installations (33)

There are at least 150 systems operating on various nickel baths, mostly utilizing cellulose acetate membrane elements and with recoveries in the range of 90 - 97%. The relatively high evaporation rate resulting from the elevated bath temperature generally allows complete recycle of the concentrate stream as well as the permeate stream.

TABLE 3.10 Recovery of Nickel by Reverse Osmosis (33)

Type of Bath	Membrane Element	Membrane Life	System Payback	Years of System Operation	Items Plated
Watts	Spiral Cellulose Acetate	2 years	12 months	4	Luggage Hardware
Watts	Spiral Cellulose Acetate	1 year	12 months	5	Wire Shelving
Watts	Spiral Cellulose Acetate	1 year	16 months	5	Wire Shelving
Watts	Spiral Cellulose Acetate	1 year	24 months	5	Steel Stamping
Watts	Spiral Cellulose Acetate	1,5 years	36 months	7	Job Shop
Watts	Spiral Cellulose Acetate	1,5 years	24 months	8	Job Shop
Watts	Spiral Cellulose Acetate	1 year	30 months	5	N/A
Watts	Spiral Cellulose Acetate	2 years	8 months	6	Electrical Devices
Watts	Spiral Cellulose Acetate	4 years	11 months	8	Plumbing Hardware
Watts	Spiral Cellulose Acetate	3 years	8 months	9	Steel Furniture
Watts	Spiral Cellulose Acetate	1,5 years	18 months	6	Electrical Devices
Bright Nickel	Spiral Cellulose Acetate	1,5 years	14 months	11	Plumbing Hardware
Bright Nickel	Spiral Cellulose Acetate	2 years	36 months	4	N/A
Bright Nickel	Spiral Cellulose Acetate	1,5 years	12 months	5	Automotive Bumpers

TABLE 3.10 (continued)

Type of Bath	Membrane Element	Membrane Life	System Payback	Years of System Operation	Items Plated
Bright Nickel	Spiral Cellulose Acetate	2 years	8 months	9	Hard Tools
Bright Nickel	Spiral Cellulose Acetate	1,5 years	20 months	8	Brass Stampings
Sulfamate	Spiral Cellulose Acetate	2 years	13 months	5	Electrical Terminals
Sulfamate	Spiral Cellulose Polyamide	1,5 years	N/A	3	P.C. Board Contacts

3.4.1.2 Copper Sulphate Installations (33)

Approximately 12 reverse osmosis systems are operating on rinses from proprietary copper foil manufacturing processes.

TABLE 3.11 Recovery of Copper by Reverse Osmosis (33)

Number of Systems	Feed Flow (m^3/h)	Membrane Element	Concentration Composite	System Recovery	Membrane Life	Years of System Operation
10	14	Hollow Fibre, Polyamide and Cellulose Triacetate	Waste Treatment	75%	1 - 3 years	5
2	9,5	Spiral wound, Thin Film Composite	Reuse	87.5%	1 year	7

Pretreatment requirements :

Hollow fibre polyamide element - 1 micron filter catridge

Hollow fibre cellulose triacetate element - 3 micron filter cartridge

Spiral wound thin film composite element - 5 micron filter cartridge

3.4.1.3 Zinc Sulphate Installations (33)

One reverse osmosis plant is operating on the zinc sulphate rinse from a proprietary copper foil manufacturing process. The system utilizes spiral wound thin film composite membrane elements with a feed rate of 10,5 m^3/h and recovery of 87.5%. Although the system has been in for more than seven years, the thin film composite element has been in for just over a year and is working well.

The concentrate stream is further reduced in volume in an evaporator (operating at 90% recovery) and returned to the bath.

3.4.1.4 Brass Cyanide Installations (33)

Approximately five reverse osmosis systems are operating on the brass cyanide rinses from a proprietary copper foil manufacturing process. Both polyamide and cellulose triacetate hollow fibre membrane elements are utilized. Feed rate is approximately 15 m^3/h per system at a recovery of 90%. The systems have been operating for five years and the membrane element life is 3 - 4 years. Pretreatment is one micron filter catridges for the polyamide elements and 3 micron filter cartridges for the cellulose triacetate elements.

3.4.1.5 Copper Cyanide Installations (33)

A reverse osmosis plant is operating at a printed circuit contact plating application in which the first flowing rinse is fed to a polyamide hollow fibre membrane element at a flowrate of approximately 50 m^3/h. The system operates at approximately 90% recovery, with a portion of the concentrate recycled to the plating bath and remainder to the waste treatment system. All of the permeate is reused in the rinse stream. The system has been operating for more than three years. Pretreatment is one micron filter cartridge followed by activated carbon. Membrane elements have lasted for 2,5 to 3 years.

At a medical device plating application with a lead brass substrate the first rinse fed to a polyamide hollow fibre membrane element. The system operates at 93% recovery, with approximately one-half of the concentrate recycled to the plating bath and the rest to the waste treatment system. All of the permeate is reused in the rinse stream. The system has been in operation for more than seven years. Pretreatment is by 1.2 micron filter cartridges followed by 0,45 micron membrane filters, and the membrane life is about 4,5 years.

3.4.1.6 Chrome Installations (33)

A copper foil manufacturer has been investigating the use of spiral wound thin film composite membrane elements for use in recovering hexavalent chrome from the rinses in a proprietary manufacturing process. Hollow fibre membrane elements lasted only 1 - 2 months before irreversible fouling, occured spiral wound elements have performed satisfactorily for over 6 months. Pretreatment consisted of 5 micron cartridge filtration.

3.4.1.7 Anodising Dye Recovery

The dye rinse water (pH 1 to 2) from the anodic oxidation of aluminium has been concentrated and recycle for a year using Teijin PBIL reverse osmosis membranes (45). The pay back period was given as 2 years. The same type membranes have been used to preconcentrate rinse water from the plating of silver, gold and brass.

3.4.2 Ultrafiltration

Ultrafiltration is a low pressure membrane filtration process used for separating macro-molecules, colloids, emulsions and suspended solids from water. A semi-permeable microporous membrane performs the separation. Water and low molecular weight solutes pass through the membrane and are removed as permeate. The feed stream flows parallel to the membrane surface. This cross-flow characteristic differs from the perpendicular flow of ordinary filtration. For ordinary filtration, a filter cake builds up on the filter septum, resulting in frequent filter replacement or cleaning. In ultrafiltration, the cross-flow conditions prevent filter cake build up and high filtration rates or fluxes can be maintained continuously.

Emulsified oils from rinse baths following degreasing (35) or phosphating tanks can be concentrated by ultrafiltration. The oily concentrate can be incinerated while the permeate can be recycled. In certain cases the alkaline cleaner will pass through the membrane and can be returned back to the process with the recovered water.

Charged membrane ultrafiltration is a technique for the separation and concentration of inorganic salts present in aqueous solutions. The Donnan exclusion mechanism is responsible for salt rejection. For a membrane containing fixed negative groups, the effect of the Donnan potential is to repel anions (co-ions) from the membrane, cations are thus rejected in order to maintain electroneutrality across the membrane. The rejection of salts is high at low salt concentrations and decreases at higher salt concentrations. This process is appropriate for industrial applications requiring water recycling and reuse in which complete water demineralisation is not warranted.

The use of Millipore PSAL membranes (negatively charged sulfonic acid functional groups) for the ultrafiltration metal salts has been described (36, 37). The projected removal of metal salts from copper smelting scrubber blowdown at the 90 and 95% water recovery is given in Table 3.12.

TABLE 3.12 Removal of Metal Salts from Copper Smelting Scrubber Blowdown

	Feed	Rejection 90% Water Recovery	Rejection 95% Water Recovery
pH	4,5		
Suspended Solids	600 mg/l		
As	100 mg/l	0,93	0,91
Se	20 mg/l	0,90	0,89
Cd	10,5 mg/l	0,77	0,73
Zn	86 mg/l	0,77	0,73
Cu	297 mg/l	0,86	0,83
Fe	149 mg/l	0,98	0,97
Pb	39 mg/l	0,98	0,97
Hg	2 mg/l	0,93	0,91
Ca	625 mg/l	0,75	0,71

The estimated net operating cost for a two stage ultrafiltration system to treat 3m3/h of rinse water (59 mg/l Ni) from a Watts nickel bath would be $720/m3 (1979). The water recovery of 91% and a nickel rejection 83% would enable both the nickel concentrate and the permeate to be recycled.

Millipore PTAL negatively-charged membranes were used to remove charged heavy metal complexes from plating effluent (46). The rejection of metal is highly dependent on the size and charge of the complex metal species. The rejections range between 77 to 96% and decrease as follows:

$Zn(CN)_4^{2-}$ > $Zn(CN)_3^{1-}$ and

$Cu(EDTA)^{2-}$ > $Cu(CN)_3^{2-}$ > $Cu(C_2O_4)^{2-1}$.

3.4.3 Cross-Flow Microfiltration (CFMF)

Cross-flow microfiltration differs from conventional barrier filtration in that the feed flow is parallel to the filter septum hence the accumulation of the solids on the filter medium can be controlled by the shearing action of the flow (38, 39, 40). Thus, CFMF offers the possibility of a quasi steady state operation with nearly constant flux when the driving pressure differential is held constant. Cross-flow microfiltration removes suspended solids whereas ultrafiltration and reverse osmosis removes macromolecules or macromolecules and ions in addition to suspended solids. The filter tubes can be constructed from porous plastic, fibre glass, sintered ceramics, metal carbon or woven fabric.

Results obtained (38) using porous plastic tubes for the filtration of effluent produced by the manufacture of lead-acid batteries indicate that the suspended solids are reduced from 150 g/l to 3 mg/l, lead from 200 mg/l to 0,1 mg/l and similar rejections for copper, nickel, zinc, arsenic and antimony. Average permeate fluxes of 40l/m2h were obtained for a water recovery of 85%, the resulting sludge contained 20-35% w/w suspended solids.

The installation of a cross-flow microfilter results in a self contained effluent clarification system that does not require the space, liquid flow or retention time associated with typical clarification systems. In a field evaluation (40) a Hydroperm system was operated in parallel with a clarifier at a metal finishing firm. The inlet pressure to the unit was 140 kPa and the feed flowrate through the tubes was 2 m/sec. The tubes were thick walled (1 mm) hollow tubes (6 mm ID) made of thermoplastic containing micron sized pores. The steady state permeate fluxes ranged from 170 to 680 l/m2h. The suspended solids in the permeate was generally below 10 mg/l and the concentration of cadmium was less than 0,5 mg/l (when the pH control was correctly maintained).

Cross-flow ultrafiltration using micro porous membranes (Nemtek) reduce dissolved metals to 0,05 mg/l. Lancy have introduced a polypropylene membrane coated with a proprietory inorganic powder and is used after sulphide precipitation to reduce metals to below 0,05 mg/l (41).

3.4.4 Electrodialysis

Electrodialysis is based on the following points :-

(a) Most of the salts dissolved in water are ionic,

(b) These positive or negatively charged salts are attracted by an opposite electrical charge, and

(c) membranes can be devised which will be selective to the type of charged ion which they will pass or reject i.e. membranes which pass anions but reject cations is an anionic-permeable membrane.

The electrodialysis process is illustrated in Figure 3.14.

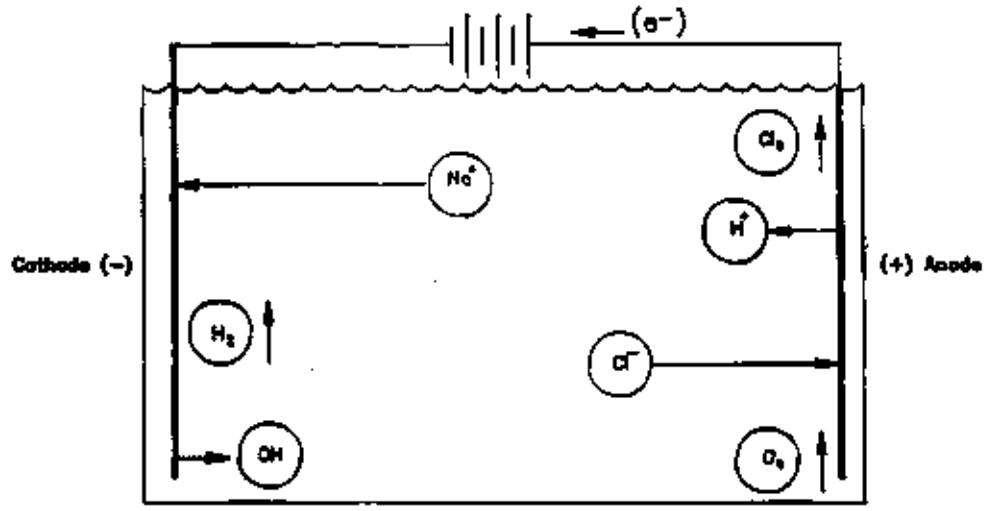


Figure 3.14 : Electrodialysis

ED membranes are flat sheets usually made of a plastic film which is bonded to a fabric backing to provide strength. Ion transfer sites are added to the membrane to give the ionic characteristics.

Two types of membranes are currently produced : homogeneous and heterogeneous. The former, made by Ionics, has sites uniformally distributed through the membrane and the latter (such as made by Mitsubishi) has discrete charge sites.

Membranes come in various sizes and a typical production size is 1 020 x 460 mm. Holes are precut in the membrane to form flow channels and assembly holes.

Several different membrane types are produced with varying charge density, susceptibility to anionic membrane fouling and tightness to water flow.

The membrane stack is illustrated in Figure 3.15 showing different stack arrangements. The stack consists of membrane sheets and spacers to give alternate concentrating and diluting cells. The number of stacks, stages and electrodes used is determined by the design.

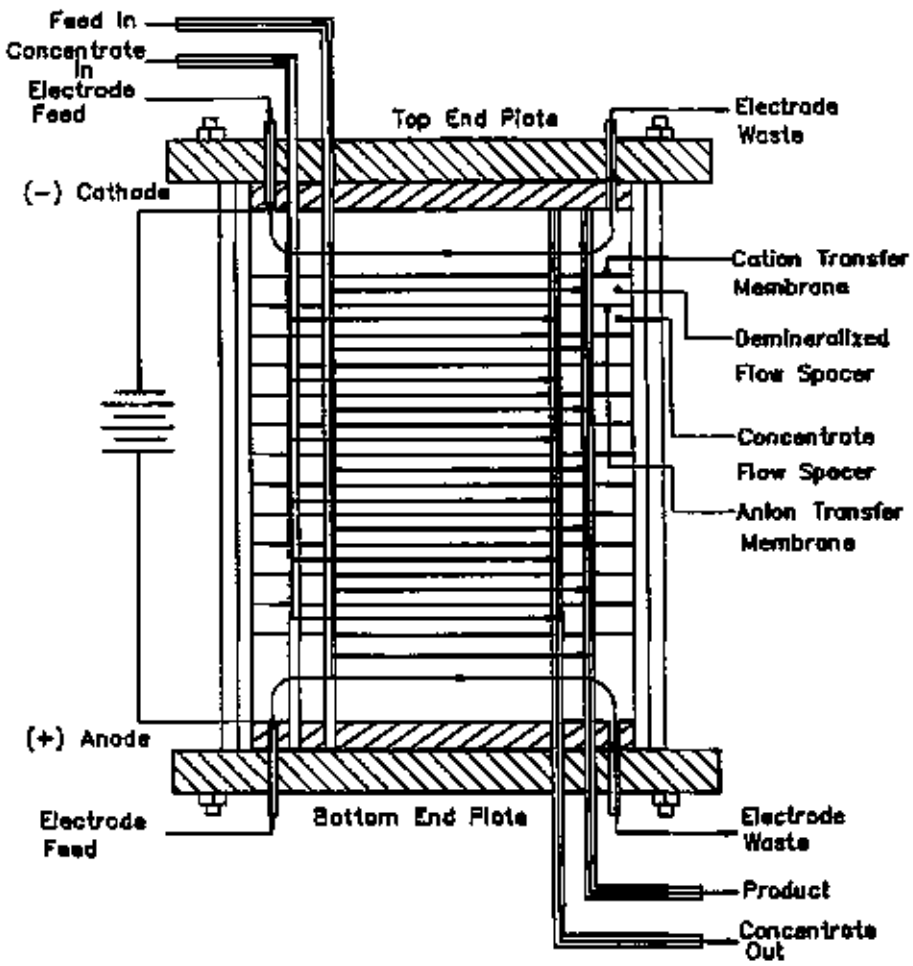


Figure 3.15 : Electrodialysis Membrane Stack

Electrodes are generally constructed of niobium or titanium with a platinum coating. Electrode reactions produce hydrogen ions and oxygen and/or chlorine gas at the anode (positive electrode) and hydrogen gas and hydroxyl ions at the cathode. A separate stream is generally used in the space next to the electrodes in each stack and the by-products of the reactions are confined to these streams.

In the electrodialysis reversal process the anode and cathode are electrically reversed several times an hour.

An electrodialysis (ED) system (41) using Ionac MA 3475 and MA 3470 membranes was used to recover and recycle copper cyanide. Limitations in the concentration ratio that could be achieved necessitated a two stage ED system linked into a two stage static rinse system. Each stage maintained a concentration ratio of 128 : 1 i.e. with a plating bath at 52,1 g/l cyanide the rinse baths operated at 407 mg/l and 3,2 mg/l respectively. All the cyanide, metal and impurities are returned to the plating bath necessitating periodic replacement or continuous purification.

The membrane flux was 1,4 l/m2h for a concentration gradient of 16 500 : 1 in a two stage system. The capital cost of the system to treat 3,78 l/h dragout was $1 600 (1973) and the total power consumption was 4 kW based on a volt drop of 6 volts per cell pair.

The electro osmotic transport of water and the transport of counter ions limit the maximum obtainable copper cyanide concentration to 85 g/l. If the plating bath were operated at an elevated temperature then evaporation losses would enable a plating bath concentration of 120 g/l copper cyanide. The use of anionic brighteners caused membrane fouling. These results would be applicable to cyanide baths of zinc, cadmium, silver and gold.

Electrodialysis has been used to recycle dragout from Watts Nickel plating baths using Neosepta membranes supplied by Tokuyama Soda Co (42). Two static dragout tanks followed the plating tank. Electrodialysis treatment of each of the static dragout tanks maintained the nickel concentration at 2-3 g/l in the first tank

and at 0,3 g/l in the second tank. The concentrate from both electrodialysis systems was returned to the plating bath. The nickel concentration in the concentrates were 52 g/l and 23 g/l respectively. The usage of raw materials and destruct chemicals were reduced by over 90%. The payback time for a system operating for 5 000 h/year would be 2,8 years.

The advantage of ED over RO is that concentration ration of 50 to 100 fold can be achieved permitting direct return of the concentrate to the plating bath with out the need for evaporation. ED is a continuous process and requires no interruption for regeneration of ion exchange material or disposal of regeneration solutions as in conventional ion exchange systems.

Teflon based ion exchange membranes (Nafion, Flemion) have enabled electrodialysis to be carried out under extreme oxidising conditions. A process has been developed by the US Bureau of Mines (43) for the one step purification and reoxidation of spent chromic acid solutions.

The effluent from the sodium dichromate/sulphuric acid pickling of brass forgings containing copper, zinc and ferric ions together with trivalent and hexavalent chrome. The cation exchange resin rejects the chromium ions while allowing the passage of mono and divalent cations. Under the influence of a dc current the metal ions are either accumulated and concentrated (zinc, iron) or plated out as metal on the cathode (copper). The lead alloy anode oxidises the trivalent chrome to hexavalent chrome as in a plating bath. The chromic solution is continuously recirculated through the cell. The installation of the system has resulted in the pickling solution lasting for over 18 months, previously it was dumped daily. The payback time was estimated to be 26 months.

A second study (28) indicated that the system exhibited a reliable performance on a continuous unattended basis over the several days of monitoring and successfully recovered and returned to the plating tank all chrome other than that plated on the work piece. The sludge production was very low. Economically the system is much more attractive than evaporation (Table 3.13).

A similar type of membrane system has been developed (44) to regenerate printed circuit board etching solutions (cupric chloride). The cation exchange membrane permits copper ions to pass through to the cathode where they are deposited; the regenerated etchant can then be recycled back to the etching line.

TABLE 3.13 Comparison of Treatment Costs (28) of Chrome Rinse Water by Evaporation and Ion Transfer

	Costs (US $ 1980)	
	Evaporation	Ion Transfer
Total Installed Cost (75 l/h)	35 850	13 000
Annual Operating Costs		
Labour	525	390
Maintenance	2 150	1 260
Plant Overheads	690	575
Steam (@ $4/10^{6}Btu)	2 020	
Cooling Water (1 000 US gal/h at $0,58 / 1 000 gal)	560	
Utilities	750	250
Replacement Membranes		500
	6 695	2 975
Annual Fixed Costs		
Depreciation (10% of investment)	3 585	1 300
Taxes and Insurance	360	130
Total Annualised Operating Costs	10 640	4 405

The savings in chemicals, water and effluent charges for both systems would be the same.

Ion-exchange membranes can be used in Donnan dialysers Figure 3.16. If solutions of to electrolytes are separated by a cation ion exchange membrane the anion composition of the two solutions must remain constant since the membrane is impermeable to anions. The cations will redistribute between the two solutions until equilibrium is reached (see 3.4.5 Coupled Transport). The US EPA is funding research into the removal of metal cyanide complex ions from electroplating process wash waters.

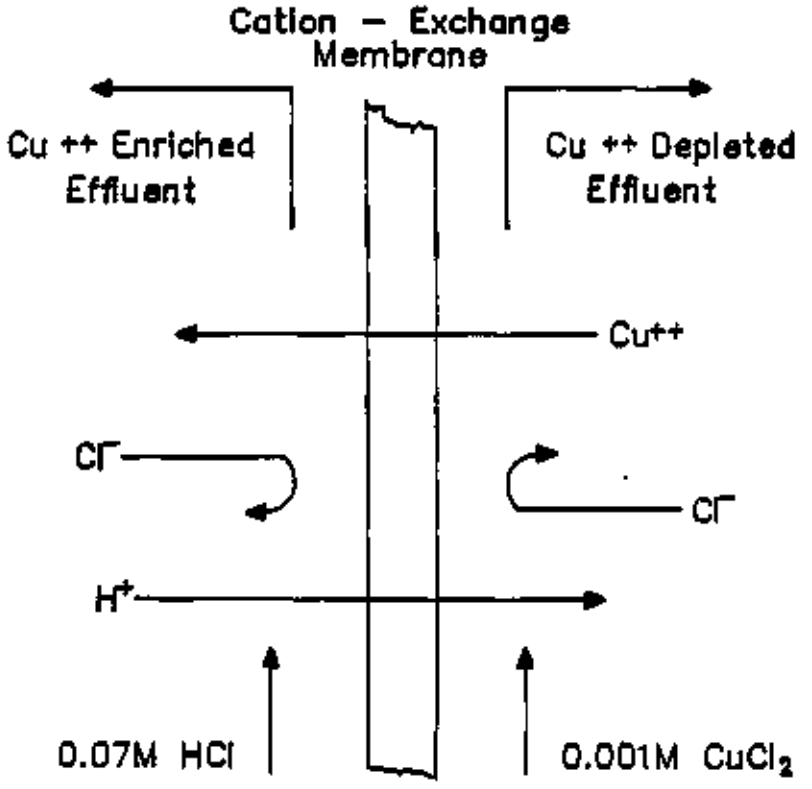


Figure 3.16 : Mechanism of Donnan Dialysis

3.4.5 Coupled Transport Systems

In a coupled transport membrane, the flow of the permeant of interest is coupled to the flow of some second species. Under the right conditions, the flow of this second species can force the permeant of interest to flow against its own concentration gradient thereby, for example, separating this species from other species and concentrating it as well. These membranes can thus be considered as a kind of selective chemical pump. Two types of membranes are available.

(i) a suitable liquid complexing agent constrained by capillary forces to the pores of a microporous membrane.

(ii) a charged semi-permeable membrane.

In the case of a liquid membrane, the liquid complexing agent is specific for the permeant of interest under certain conditions. The desired permeant is complexed at one interface of the membrane and the external solution. The complex diffuses across the liquid membrane to the downstream interface where the reaction is reversed because of some appropriate change in conditions . The free complexing agent then diffuses back across the membrane where it picks up more of the desired permeant. The complexing agent thus acts as a shuttle, carrying both the desired permeant and some second, coupled species across the membrane.

In the recovery of metals the coupled species is the hydrogen ion. This ion can either cross the membrane in the same direction as the metal of interest (co-transport) or opposite to the metal ion (counter-transport). Because of the requirement to maintain electro neutrality across the membrane, the hydrogen ion must move in the same direction as the metal ion if the metal is present in the anionic form eg. chromium as chromate. On the other hand with free metal ions such as copper or nickel in solution, the flow of hydrogen ions must be counter the flow of metal ions.

Tests were carried out (45, 46) on a range of complexing liquids to determine membranes and conditions that would be suitable for plating effluents containing chromium, copper and nickel.

Substantial savings could be realised for chromium recovery, copper recovery would be marginally economic while nickel recovery would not be economic. The complexing liquid in these cases was a tricaprylyl amine. (Alamine 336, Henkel).

The payback time for various chromium recovery systems has been calculated to be:-

3,9 years - coupled transport
5,2 years - ion exchange
4,9 years - evaporation

At that time R.O. was not suitable for chromium recovery however the payback time for the recovery of nickel plating effluents by RO was calculated to be 4,3 years.

3.5 Activated Carbon

Activated carbon has been used to remove heavy metals such as copper, cadmium, iron (3), chrome (6) and chrome (3) (49, 50, 51).

Hexavalent chrome is both adsorbed and reduced on activated carbon. The maximum Cr(6) adsorptive capacity is at pH 2,5 and decreases rapidly between pH 2,5 and 7,1. Below pH 2,5 the Cr(6) is reduced to Cr(3).

If the pH conditions are unfavourable for Cr(6) to Cr(3) reduction, then the chrome can be eluted from the carbon with caustic soda and recycled.

The adsorptive capacity of the carbon was in the range 870-180 mole/g for a pH range of 2,5-6,5. The carbon dose required to remove 99% of a sodium chromate solution as a function of solution concentration and pH is shown in Figure 3.17 (the rate of adsorption to reduction is 50 : 1).

Elution of the carbon with 34 bed volumes of 1 Molar caustic soda resulted in a 3,8 Molar Cr(6) stream which represented a concentration factor of 38 for a feed condition of 1×10^{-3} M Na_2CrO_4. The carbon losses were estimated at 2% per cycle.

The chemical cost (1979) to reduce 34 m^3/day of 168 mg/l of disodium chromate were given as $0,51 for sulphur dioxide and $0,46 for activated carbon.

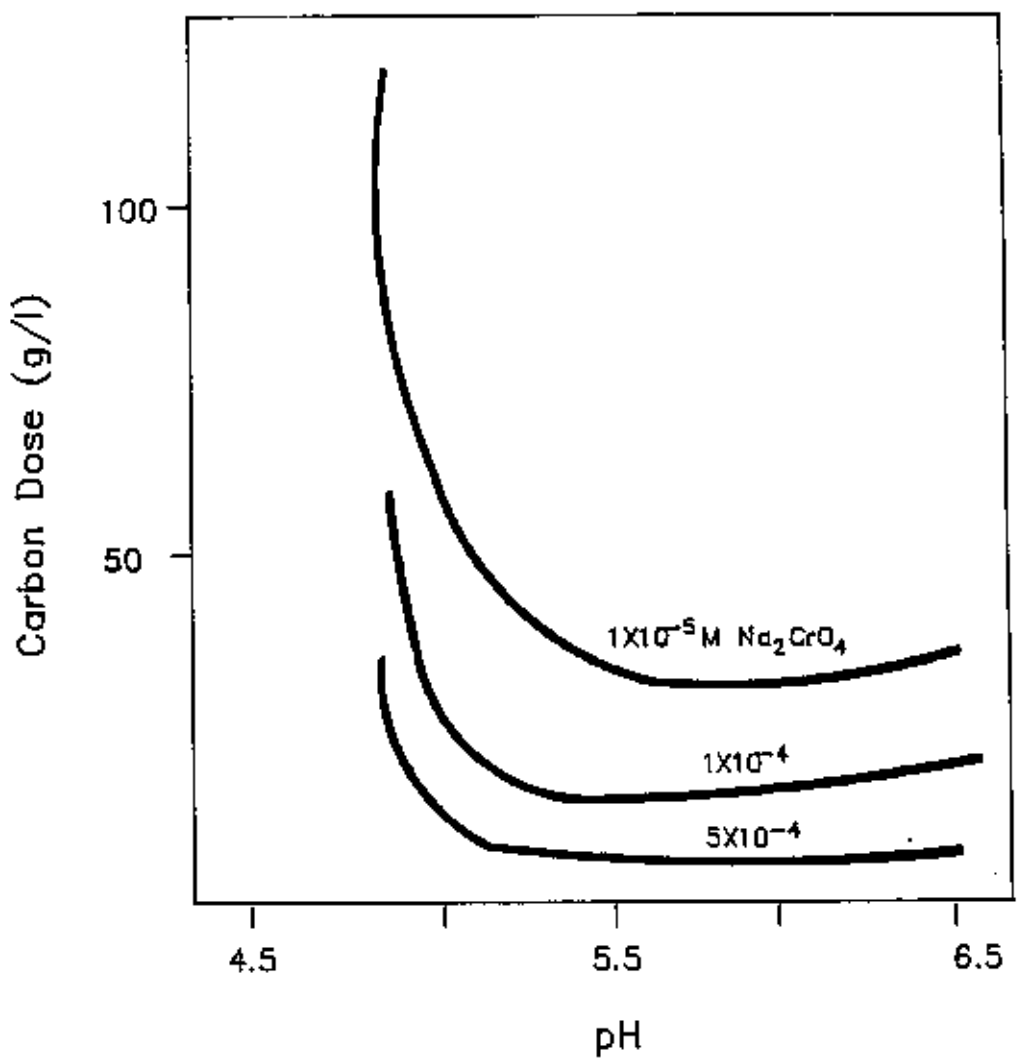


Figure 3.17 : *The carbon dose required for 99% treatment of a 1×10^{-3} M Na_2CrO_4 solution as a function of pH and Na_2CrO_4 in the head reactor*

3.6 Ion Exchange

Ion exchange is a versatile separation process with potential for broad application in the metal finishing industry (52), both for raw material recovery and reuse and for water pollution control. Three main areas of application have been demonstrated:

(a) wastewater purification and recycle
(b) end-of-pipe pollution control
(c) chemical recovery

Ion exchange units are compact and easy to automate compared to conventional precipitation systems.

3.6.1 Water Purification and Recycle

Mixed rinse solutions are treated to permit reuse of the treated water. The contaminants in the rinses are concentrated into the small volume purge streams and are thereby made more economical to treat. Advantages of ion exchange are that it separates dilute solutions of ionic compounds from water solutions. The process can provide high purity water over a broad range of loading conditions. The resins are durable in severe chemical environments.

3.6.2 End-of-Pipe Pollution Control

Ion exchange is used to remove only the toxic heavy metals and metal cyanide complexes from combined waste streams before discharge. The non-toxic ionic compounds are allowed to remain in solution. This process can either follow conventional hydroxide precipitation to lower the metal concentration in the discharge or else it can be used to directly treat wastewaters to remove heavy metals and metal cyanide pollutants.

TABLE 3.14 Amine-Borane Resin Selectivity for Metal Ion Species

Reactive		Non-reactive	
Metal Ion	Source	Metal Ion	Source
Au^{3+}	$AuCl_4^-$	Group 1A	Chloride salts
Pt^{2+}	$PtCl_4^-$	Group 11A	Chloride salts
Pt^{4+}	$PtCl_6^-$	Group 111A	Chloride salts
Pd^{2+}	$PdCl_2$	Group 1VA	Oxides & nitrates
Ag^+	$AgNO_3$	Cr^{3+}	$CrCl_3$
Ir^{3+}	$IrCl_2$	Mn^{2+}	$MnCl_2$
Rh^{3+}	$RhCl_2$	Fe^{2+}	$FeCl_2$
Hg^{1+}	Hg_2Cl_2	Fe^{3+}	$FeCl_3$
Hg^{2+}	Hg_3Cl_2	Co^{2+}	$CoCl_2$
CH_2Hg^+	CH_3HgCl	Ni^{2+}	$NiCl_2$
As^{3+}	As_2O_3	Cu^+	$CuCl$
Sb^{3+}	Sb_2O_3	Cu^{2+}	$CuCl_2$
Bi^{3+}	$Bi(NO_3)_3$	Zn^{2+}	$ZnCl_2$
		Cd^{2+}	$CdCl_2$
		Ru^{3+}	RuCl
		Sn^{4+}	$SnCl_4$
		Pb^{2+}	$Pb(NO_3)_2$
		Tl^{3+}	$Tl(SO_4)_3$

TABLE 3.15 Saturated Capacities of Amine-Borane Resins

Metal	Source	Grams of metal per g of dry resin
Platinum	K_2PtCl_6	0,6
Platinum	K_3PtCl_4	1,2
Gold	$HAuCl_4$	0,8
Palladium	$PdCl_2$	0,64

Conventional hydroxide precipitation is usually sufficient treatment to comply with most discharge regulations however when unusually strict limits are placed on effluent metal concentrations or where metals are complexed with chemical constituents that interfere with their precipitation as metal hydroxides, conventional treatment may not be reliable for compliance with the discharge limits. Ion exchange can provide a relatively inexpensive method for upgrading the system performance.

Ion exchange has been used in a limited extent to remove the toxic pollutants selectively from an untreated wastewater while allowing most of the non-toxic ions to pass through. Heavy metals and other divalent cations can be removed from a stream with a high concentration of sodium ions with a weak acid cation resin. Heavy metals can be removed from a stream containing sodium, calcium and magnesium ions with a heavy-metal-selective weak acid or chelating cation exchange resin.

Heavy metal and metal cyanide complex ions can be removed from solution while allowing most of the wastewater ionic components to pass through by a stratified bed containing strong and weak acid cation and strong base anion resins.

3.6.3 Chemical Recovery

In the chemical recovery application, segregated plating rinse waters are treated to concentrate the plating chemicals for recycle to the plating bath, the purified rinse waters are also recycled. This method is suitable when the rinse water feed has a relatively dilute concentration of plating chemicals and a relatively low degree of concentration is required for recycle of the concentrate. Ion exchange has been demonstrated commercially for the recovery of plating chemicals from acid-copper, acid-zinc, nickel, tin, cobalt and chromium plating baths. The process has also been used to recover spent acid solutions and to purify plating solutions for longer service life. The payback time for the treatment of a chromic acid bath would be 5,2 years.

A new class of Amine borane resins have been developed for the recovery of precious metals (53). These resins are mild reducing agents and they combine high capacity (Table 3.14) with excellent selectivity (Table 3.15) for precious metals in the presence of base metals. The ionic metals are removed from the solution by redution and immobilized within the porous resin head. The metals are recovered by roasting the resin at 500 - 800°C in the presence of air.

3.7 Electrolytic Process

Electrolytic techniques can be used to plate out dissolved metals, oxidise cyanide or reduce chromium from waste waters. Electrical power needed to supply the current is the major operating cost and no chemical treatment is required. The major problem is that dilute solutions of electrolytes have a high electrical resistance consequently treatment of dilute waste streams becomes prohibitive because of high electricity costs. Recent investigations have therefore, centred on development of an electrolytic method that could treat dilute solutions and overcome the high electrical resistance of the cell. The use of low voltages in plating baths is a common method of plating out unwanted ions and hence renovating plating solutions.

Electrochemical reduction units (54) for chromium reduction use consumable iron electrodes and an electrical current to generate ferrous ions which react with hexavalent chromium to produce trivalent chromium. The reaction occurs rapidly and requires minimum retention time. The level of hexavalent chromium leaving the reactor can be maintained below 0,05 mg/l. The pH of the effluent usually increases by 0,5 to 1 unit because of the generation of hydroxide ions. The chemical reduction system has a combined treatment and sludge disposal cost greater than electro chemical system when the influent hexavalent chromium concentration exceeds 5 mg/l.

A demonstration plant using carbon fibres for the removal and recovery of heavy metals and simultaneous cyanide oxidation is being evaluated by the US EPA (54). Another demonstration project involves the use of semi conductive carbon particles (to reduce

electrical resistance) for the reduction of chromium and oxidation of cyanide in separate cells.

The Electricity Council Research Centre (UK) (55) has developed the Chemelec cell which enables cations such as copper, nickel, nickel-iron, zinc, cadmium, cobalt, silver and gold to be recovered from the first static dragout tank. The fluidised bed promotes mixing in the cell and thus enables the concentration of heavy metal in the dragout tank to be maintained at 100 - 250 mg/l. The total power requirements of the unit amounts to 7,5 - 20 kWh/kg metal recovered. The recovered metal can either be reused in plating or sold as scrap. Other types of cathodes such as porous copper, iron or carbon are also available.

3.8 Biological Methods

Bacteria similar to those used to extract metals from ores are being used in pilot tests for the recovery of metals from plating rinse water (44). Cadmium and lead are bioaccumulated by the micro organisms, which are separated from the effluent and is burned to recover the elemental metal.

3.9 Sludge Handling

As far as the disposal of sludges to land fill sites are concerned the only common plating compounds that are included in the EPA Extraction Procedure toxicity limits are cadmium, chromium and lead (56). The other metal sludges are considered safe for disposal in land fill sites.

The cost of disposing of sludges is very much greater than disposing of solids consequently sludge dewatering is necessary after ; any precipitation process. The EPA has published a comparison (56) of the following types of mechanical dewatering equipment :

pressure filters
vaccum filters
centrifuges
compression filters

Table 3.16 compares some of the characteristics of the different equipment types. Table 3.17 summarises the performance of different dewatering systems for metal finishing sludges in industrial applications. In general a filter press is the most costing effective equipment for the dewatering of metal finishing sludges.

TABLE 3.16 Dewatering Equipment for Electroplating Sludge: Typical Performance Characteristics

Equipment	Feed		Solids retention (% by weight)[a]	Cake solids concentration (% by weight)	Installed cost ($1,000)[b]
	Rate (gal/min)	Solids (% by weight)			
Filter press	2-250	1-5	95-99	20-50	20-200
Vacuum filter	1-250	3-10	90-99	15-40	30-150
Precoat vacuum filter	1-250	0.5-3	95-99	20-50	30-150
Basket centrifuge	2-60	2-5	50-95	5-25	20-175
Pressure belt filter	5-200	2-6	90-95	20-40	40-200

[a]Feed solids in sludge cake.

[b]1981 dollars. Includes auxiliary equipment.

TABLE 3. 17 Performance of Dewatering Equipment for Electroplating Sludge

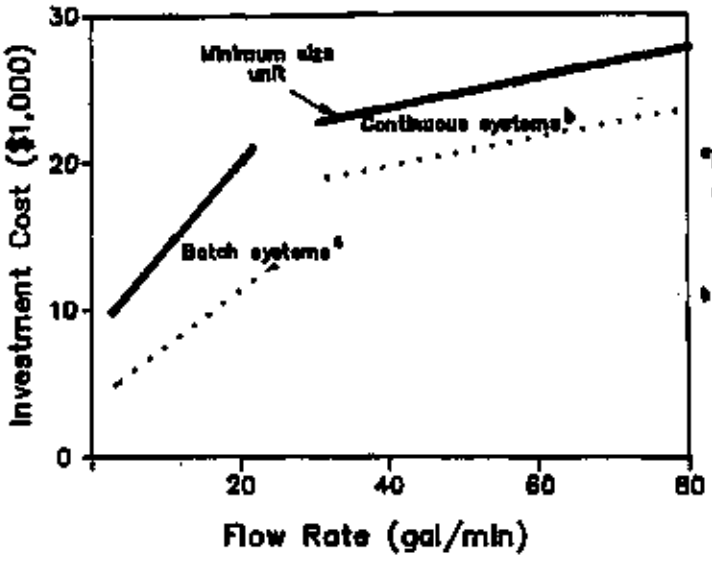
Equipment type and unit size	Sludge feed rate (gal/h)	Solids (% by weight)		Comment
		Feed	Cake	
Recessed plate filter press				
8.5-ft³ sludge-holding capacity	95	3	30	NA
10-ft³ sludge-holding capacity	300	1-2	30	Plastic-plating lime sludge
12.5-ft³ sludge-holding capacity	NA	NA	40	Chromium hydroxide dewatering
21-ft³ sludge-holding capacity	825	5	35-40	Operation attention 2-h shift; unit cleaned every 6-8 wk with recirculated 50% HCl
280-ft³ sludge-holding capacity	12,000	3-6	30	Heat-treated zinc hydroxide sludge
Vacuum filter[a]	NA	3-5	70-75	Metal oxide waste treatment sludge
Rotary precoat vacuum filter:				
9.4-ft² filtration area	100-150	NA	15	Low maintenance
37.7-ft² filtration area	330	1-5	30	Cloth life 1 yr; repairs <$200/yr
Basket centrifuge:				
1-gal bowl capacity	120	3	12-20	Satisfactory performance, low maintenance
4-gal bowl capacity	120-150	5	18	High maintenance
Pressure belt filter: 9.8-ft-wide sludge-holding capacity	900	2-6	NA	Aluminum hydroxide sludge

[a]Unit size not available.

Note.—NA = not available.

3.10 Capital Cost of Effluent Treatment Systems

The capital costs of waste water treatment alternatives for the electroplating industry have been determined by the US EPA (14, 55, 56) and are reproduced in Figures 3.19 - 3.29



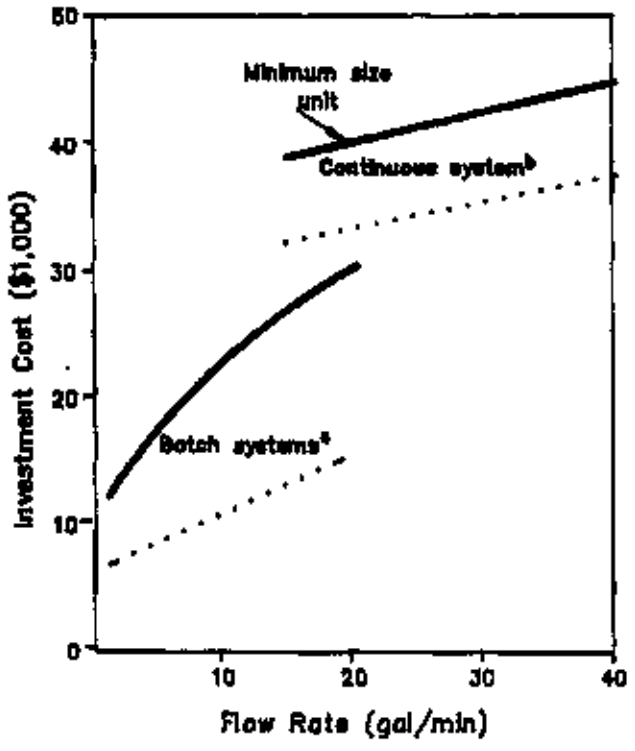
Legend :
——— total installed investment
· · · · hardware cost

[a] Installed cost is twice hardware cost; system consists of two 4-hour reaction tanks and necessary auxiliaries.

[b] System pictured in Figure 1; hardware cost for package system equals 80% of installed cost.

Note: —Cost basis, July 1978.
SOURCE: Equipment vendor.

Figure 3.19 : *Investment Cost for Chromium Reduction Units*



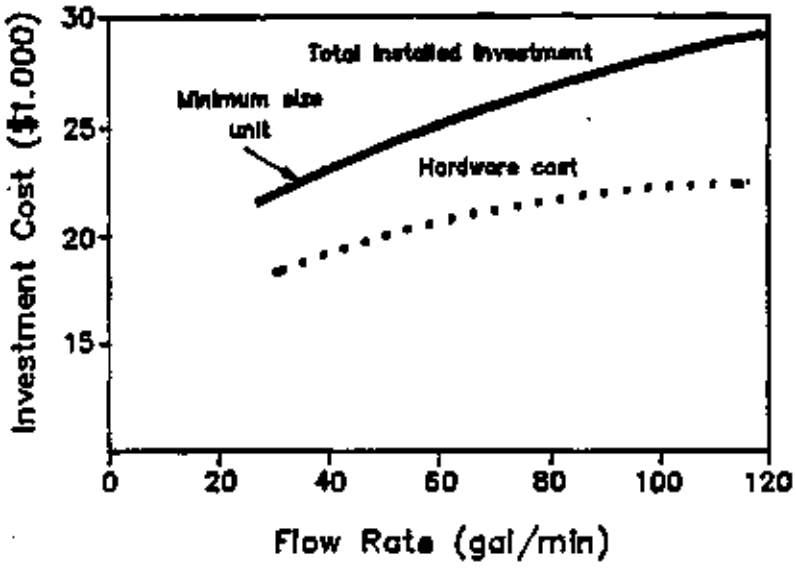
Legend:
——— total installed investment
· · · · hardware cost

[a] Installed cost is twice hardware cost; system consists of two 4-hour reaction tanks and necessary auxiliaries.

[b] System pictured in Figure 1; hardware cost for package system equals 80% installed cost.

Note: —Cost basis, July 1978.
SOURCE: Equipment vendor.

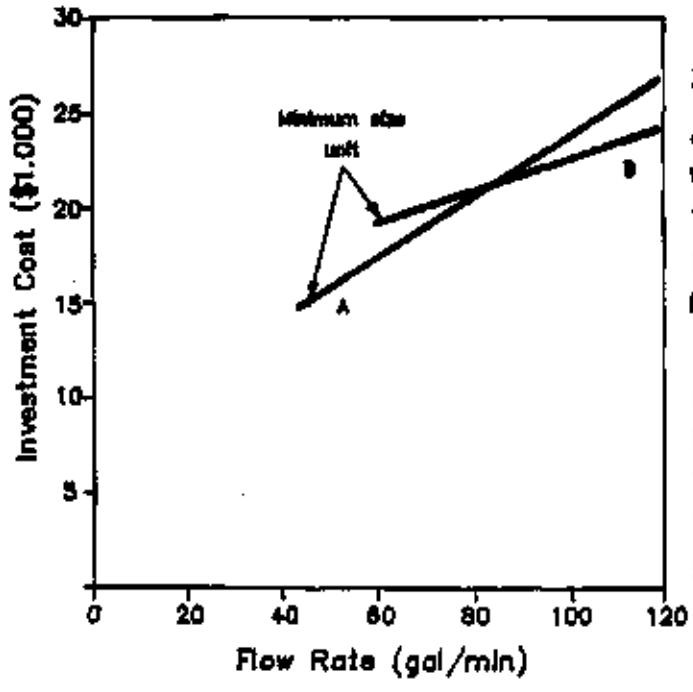
Figure 3.20 : *Investment Cost for Cyanide Oxidation Units*



Notes.—Cost basis, July 1978. Hardware cost for package system equals 80% of installed cost.

SOURCE: Equipment vendor.

Figure 3.21 : Installed Cost for Continuous Single-Stage Neutralization/ Precipitation System



Legend:

A = rectangle mixer clarifier with automatic sludge draw-off

B = plate-type clarifier with flocculating chamber

Notes.— Cost basis, July 1978. Hardware cost for these units equal 80% of investment cost.

SOURCE: Equipment vendor.

Figure 3.22 : Installed Cost for Flocculation/Clarification System

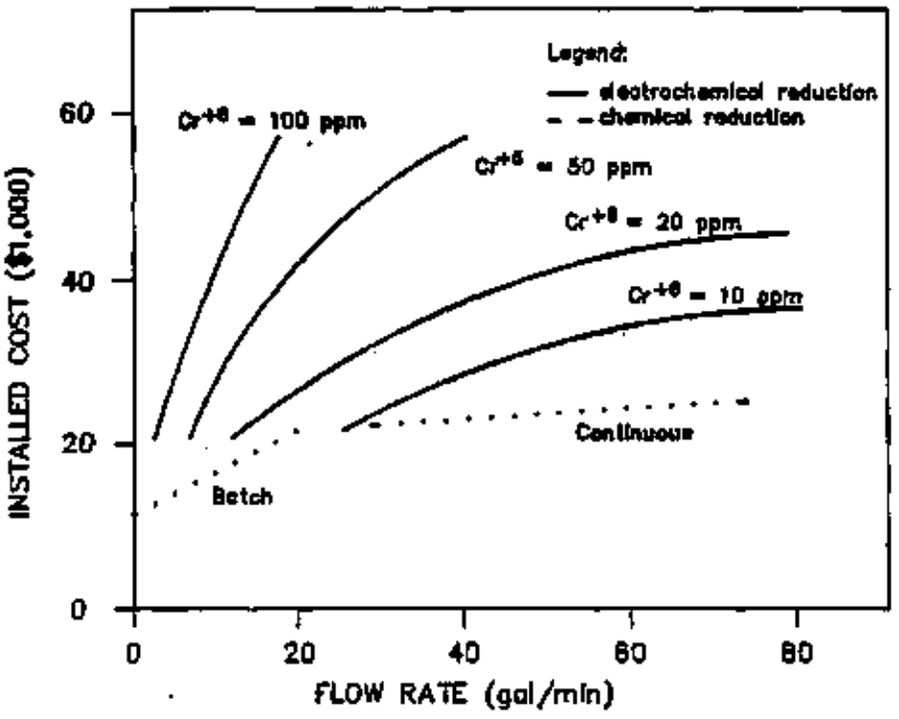
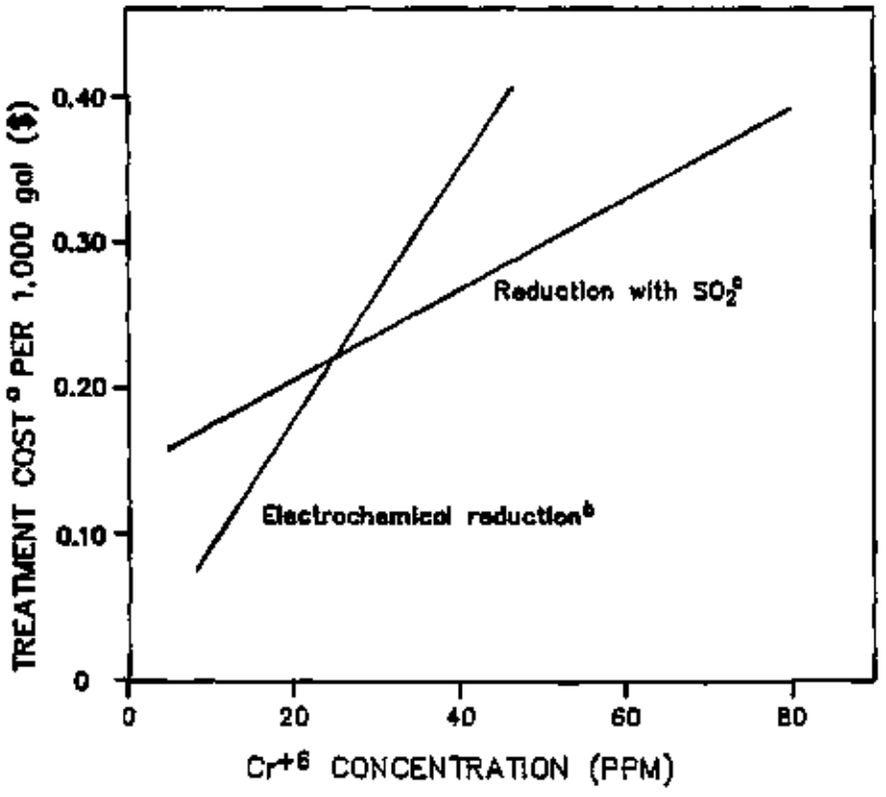


Figure 3.23 : *Installation Cost Comparison of Electrochemical and Chemical Chromium Reduction Units*

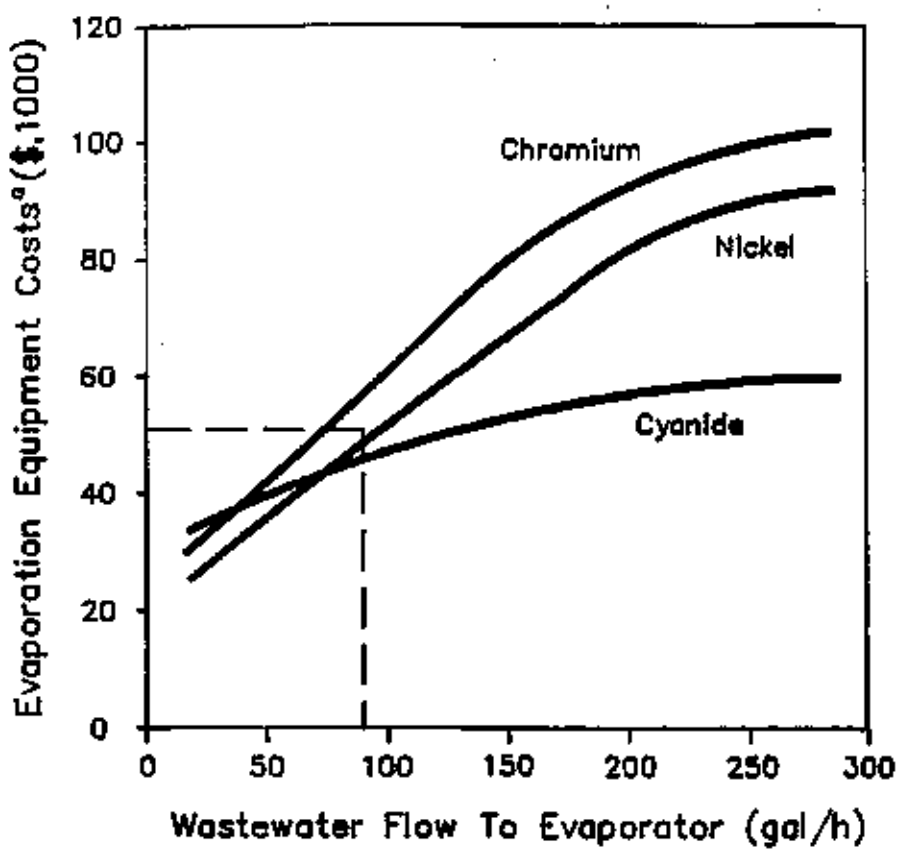


[a] Excludes pumping and sludge disposal costs.

[b] Based on $0.07 for replacement electrodes and $0.02 for electricity for each 10 ppm treated.

[c] From Figure 11.

Figure 3.24 : *Treatment Cost Comparison of Electrochemical and Chemical Chromium Reduction Units*

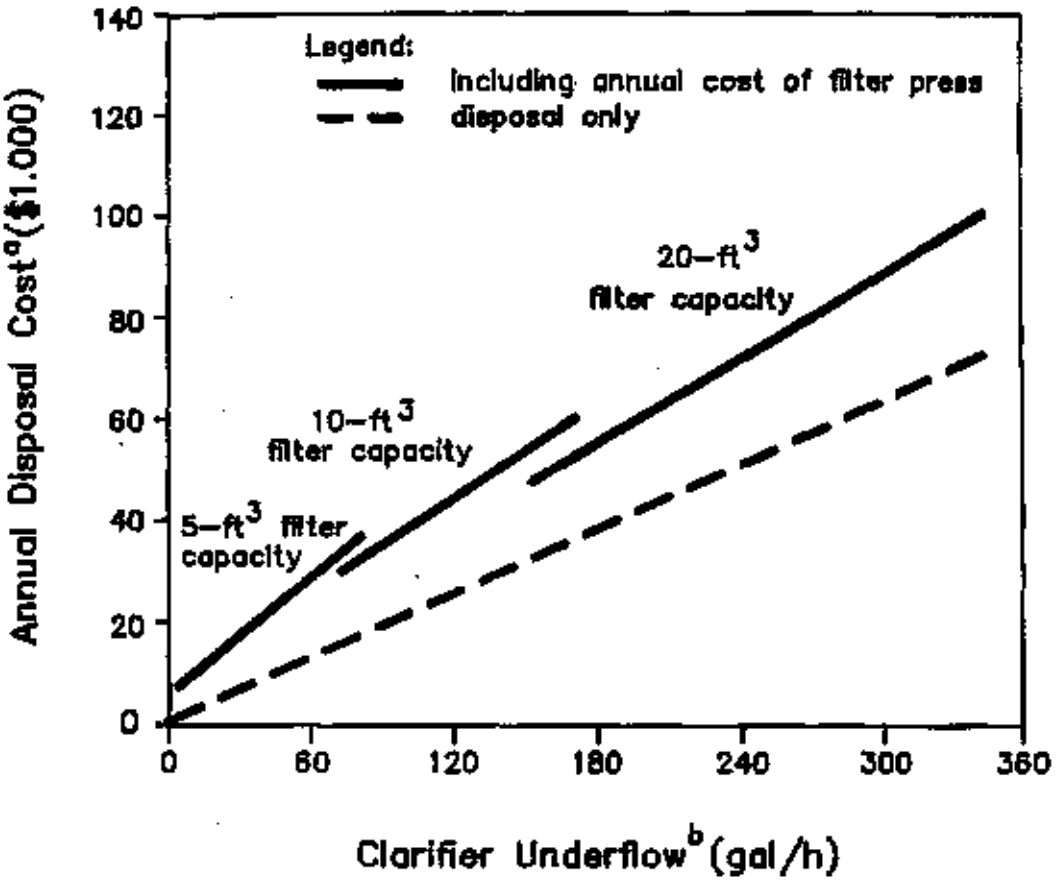


[a] Total installed costs are approximately 10% to 25% higher than equipment costs.

Note:-

Submerged tube evaporators cost approximately 30% less than rising film evaporators.
Example: A 90 gal/h rising film evaporator for nickel plating processes costs approximately $48,000 and another $10 000 to install.
A submerged tube evaporator costs approximately $34,000 and $7,000 to install.

Figure 3.25 : *Capital Cost of Single-Effect Rinsing Film Evaporators*

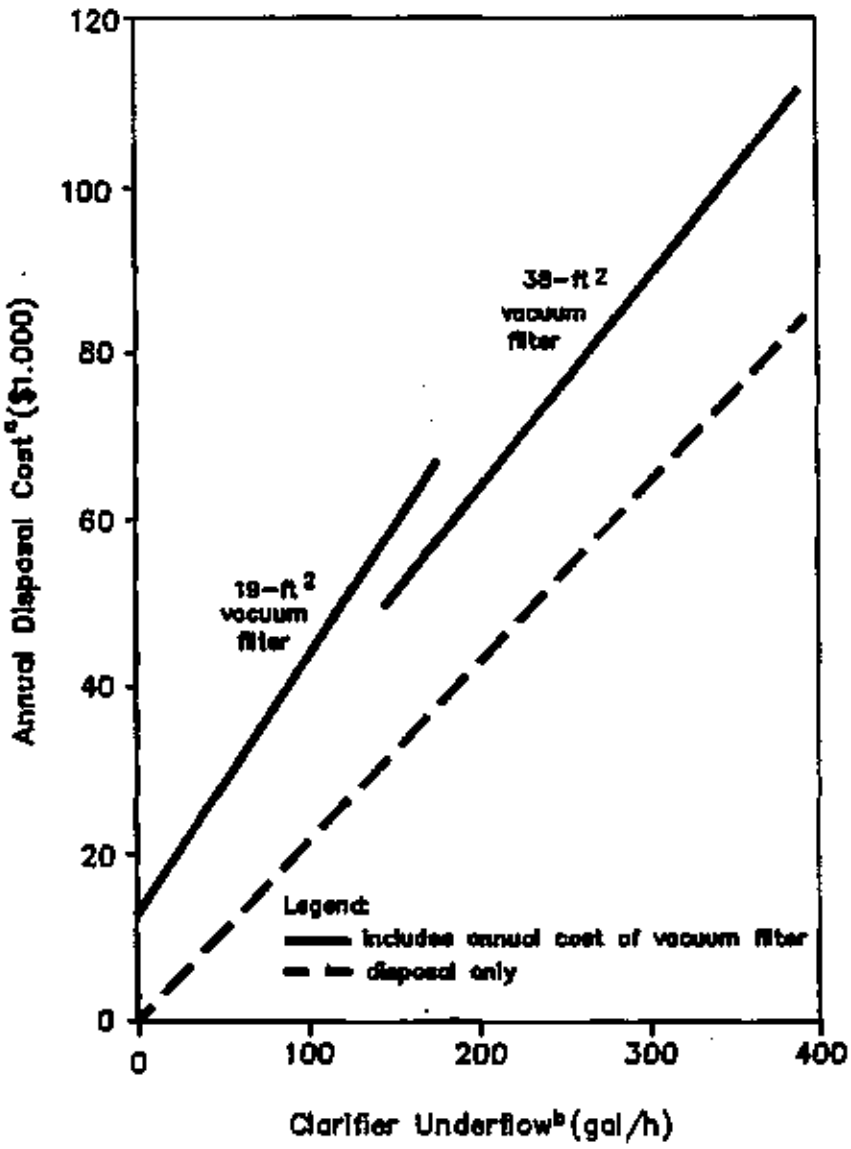


[a] At $0.43/gal. Sludge dewatered to 25% solids by weight.

[b] At 3% solids by weight.

Note—4,800—h/yr operation.

Figure 3.26 : *Filter Press Dewatering Systems : Annual Sludge Disposal Costs*



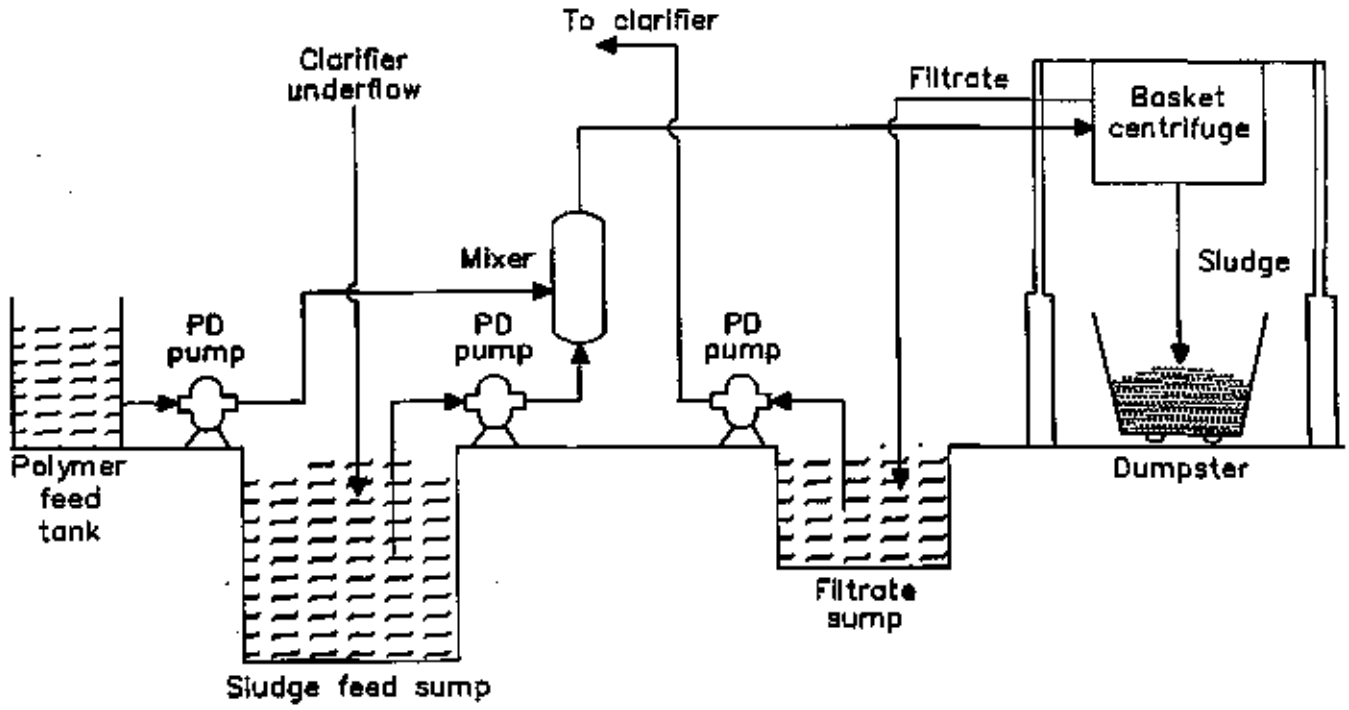
[a] At $0.43/gal for bulk 40,000-lb truckload shipped 300 mi to landfill. Sludge dewatered to 25% solids by weight.

[b] At 3% solids by weight.

Note—4,800-h/yr operation.

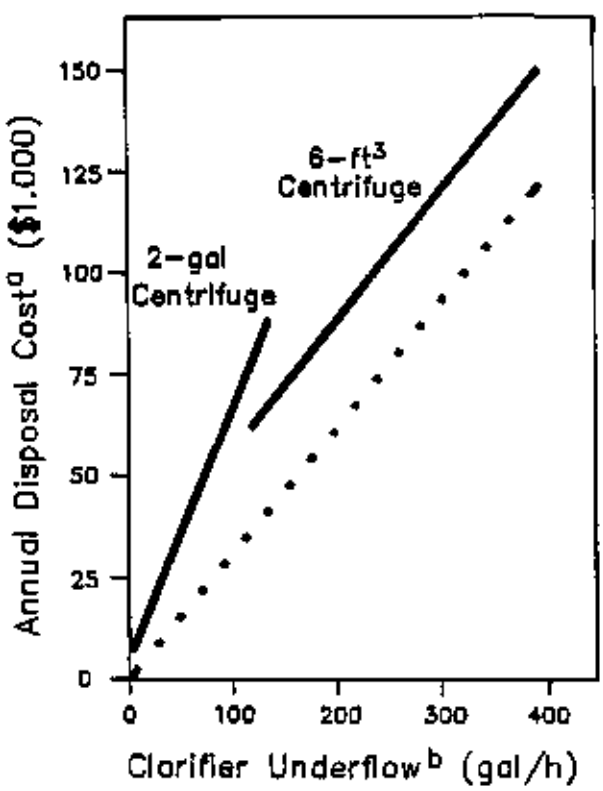
Figure 3.27 : *Rotary Vacuum Filters : Annual Sludge Disposal Costs*

(a)



Note.– PD = positive displacement

(b)

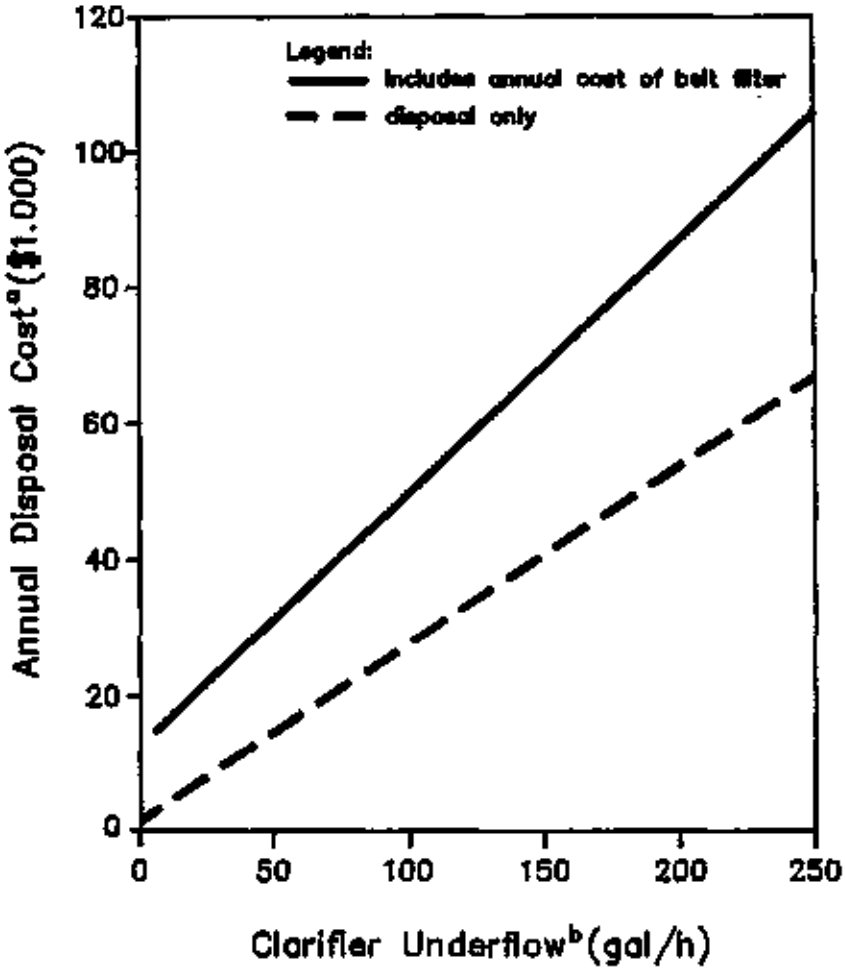


Legend:
——— Includes annual cost of centrifuge
– · – Hauling and disposal only

At $0.43/gal. Sludge dewatered to 20% solids by weight.
At 3% solids by weight.

Note.– 4,800– h/yr operation.

Figure 3.28 : *Basket Centrifuge Systems: (a) Dewatering System with Auxiliary Equipment and (b) Annual Sludge Disposal Cost*



[a] At $0.43/gal. Sludge dewatered to 20% solids by weight.
[b] At 3% solids by weight.
Note.—4,800—h/yr operation.

Figure 3.29 : Pressure Belt System : Annual Sludge Disposal Cost

3.11 Summary of the Applicability of Treatment/Recycle Techniques

A summary of suitable treatment/recycle techniques is given in Table 3.18.

TABLE 3.18 Metal Finishing Processes and Effluent Treatment/Recycle Techniques

Process	Treatment Technique	Application		
		Effluent Treatment	Water Recycle	Chemical Recycle
Sand blasting Tumbling Polishing Buffing	settling	x		
	filtering	x	x	x
Chemical Cleaning	settling	x		
	solvent skimming	x		
	oxidation of cyanide	x		
	neutralisation	x		
	ultrafiltration	x	x	
	ion exchange	x		x
Anodizing	neutralisation	x		
	reverse osmosis	x	x	x

TABLE 3.18 (continued)

Process	Treatment Technique	Application		
		Effluent Treatment	Water Recycle	Chemical Recycle
Chrome plating	reverse osmosis	x	x	x
	electrochemical	x		x
	chrome reduction	x		
	precipitation of chrome	x		
	settling/filtratiom	x		
	activated carbon	x		x
	cementation (chrome reduction)	x		
	integrated system	x		
	ion exchange	x	x	x
	evaporation	x	x	x
	electrodialysis	x	x	x
	Donnan dialysis	x	x	x
Acid copper	precipitation of copper	x		
	electrochemical	x		x
	neutralisation	x		
	ion exchange	x		x
	settling/filtration	x		
	cementation	x		
	integrated system	x		
	reverse osmosis	x	x	x

TABLE 3.18 (continued)

Process	Treatment Technique	Application		
		Effluent Treatment	Water Recycle	Chemical Recycle
Acid nickel	neutralisation	x		
	precipitation of nickel	x		
	electrochemical	x		x
	settling/filtration	x		
	integrated system	x		
	reverse osmosis	x	x	x
	electrodialysis	x	x	x
	ion exchange	x	x	x
Acid zinc	neutralisation	x		
	chemical percipitation	x		
	settling/filtration	x		
	reverse osmosis	x	x	x
	ion exchange	x		x
	electrochemical	x		x
Zinc cyanide	chemical oxidation of cyanide	x		
	precipitation of zinc	x		
	settling/filtration	x		
	electrochemical	x		x
	integrated system	x		
	reverse osmosis	x	x	x
	electrodialysis	x	x	x

TABLE 3.18 (continued)

Process	Treatment Technique	Application		
		Effluent Treatment	Water Recycle	Chemical Recycle
Cadmium cyanide	chemical oxidation of cyanide	x		
	precipitation of cadmium	x		
	settling/filtration	x		
	electrochemical	x		x
	integrated system	x		
	electrodialysis	x	x	x
Copper cyanide	neutralisation	x		
	chemical oxidation of cyanide	x		
	precipitation of copper	x		
	settling/filtration	x		
	integrated system	x		
	electrochemical	x		x
	reverse osmosis	x	x	x
	electrodialysis	x	x	x
	evaporation	x	x	x
	Donnan dialysis	x	x	x

TABLE 3.18 (continued)

Process	Treatment Technique	Application		
		Effluent Treatment	Water Recycle	Chemical Recycle
Electropainting	ultrafiltration	x	x	x
Silver plating	cementation	x		x
	ion exchange	x	x	x
	reverse osmosis	x	x	x
Watts Nickel	reverse osmosis			
General factory effluent	oxidation of cyanide	x		
	reduction of chrome	x		
	neutralistion	x		
	precipitation of metals	x		
	hyperfiltration	x	x	
	ion exchange	x	x	
	evaporation	x	x	
	activated carbon	x	x	
	ultrafiltration	x	x	
	cross-flow microfiltration	x		

TABLE 3.18 (continued)

Process	Treatment Technique	Application		
		Effluent Treatment	Water Recycle	Chemical Recycle
Chromic acid	evaporation	x	x	x
	electrodialysis	x	x	x
	Donnan dialysis	x	x	x
	ion exchange	x	x	x
	activated carbon	x		x
	electrochemical	x	x	x

CHAPTER 4. LITERATURE SURVEY - EFFLUENT DISCHARGE LEGISLATION

4.1 U.S. Environmental Protection Agency Regulations

The United States Environmental Protection Agency (EPA) has prepared detailed regulations and established administrative procedures for carrying out the laws covering the pollution control requirements for wastewater and solid residues (57, 58). The goals of the Clean Water Act of 1972 and 1977 were:

(a) eliminating the discharge of pollutants to waterways by 1985

(b) providing for fishable, swimmable waters by 1983

(c) eliminating the hazards of toxic compounds.

The electroplating industry was classified according to Table 4.1. Three levels of control were established, viz:

Best Practical Control Technology Currently Available	(BPT)
Best Available Technology Economically Achievable	(BAT)
New Source Performance Standards	(NSPS)

These standards were applicable to plating firms discharging directly to a waterway and are considered minimum standards and even more stringent requirements could be invoked for a particular water course if necessary.

BPT was the base level of control and had to be installed by July 1977, the more stringent level (BAT) had to be installed by July 1983 (later amended to 1984), while NSPS were to be established for new plants.

BPT limitations are given in Tables 4.2 to 4.4 but they have been suspended indefinitely. BAT regulations are in preparation but have not yet been promulgated.

The EPA has also drawn up pretreatment standards for electroplaters discharging into Publicly Owned Treatment Works (POTW). They were intended to :-

(a) prevent the introduction into a POTW of pollutants that will interfere with its operation,

(b) prevent the introduction into a POTW of pollutants that will pass through or otherwise be incompatible with the treatment works,

(c) improve opportunities to recycle and reclaim municipal and industrial wastewaters and sludges.

Table 4.5 gives the limits for existing electroplating facilities, more lenient standards were adopted for facilities discharging less than 10 000 gal/day (37,8 m3/day). For facilities discharging over 10 000 gal/day two alternative standards (Tables 4.6 and 4.7) could be adopted after agreement between the POTW and the industrial user.

An amendment covering an extension for innovative technology has been passed to encourage wastewater reuse and recycling as well as other innovations. It provides an opportunity for temporary relief from some guidelines to parties interested in pursuing innovative control technology if it will achieve significantly greater effluent reduction than BAT at a similar cost. The system must have potential for industry-wide application.

A range of tax incentives for financing alternatives have been made available by the Federal Government to ease the burden of compliance with environmental regulations.

TABLE 4.1 U.S. EPA Classification of Electroplating Industry

Subpart	Description
A	Electroplating of common metals (Al, Cd, Cu, Cr, Fe, Ni, Sn, Pb, Zn, and any combination)
B	Electroplating of precious metals Au, In, Pt, Rh, and Ag)
C	Electroplating of specialty metals
D	Anodizing (anodizing, acid cleaning, and alkaline cleaning)
E	Coatings (colouring, chromating, phosphating, stripping, immersion plating, acid cleaning, and alkaline cleaning)
F	Chemical etching and milling (chemical milling, etching, bright dipping, acid cleaning, and alkaline cleaning)
G	Electroless plating
H	Printed circuit board manufacturing

Note: Subparts A, B, and C may involve stripping, colouring, phosphating, acid cleaning, and alkaline cleaning.

TABLE 4.2 U.S. EPA Best Practicable Control Technology Currently Available Effluent Limitations[a] (Suspended Indefinitely[b]) : Subparts A and D-F[c]

Effluent characteristic	Effluent Limis							
	Subpart A		Subpart D		Subpart E		Subpart F	
	Daily Max	30-d Ave	Daily Max	30-d Ave	Daily Max	30-d Ave	Daily Max	30-d Ave
Pollutant (lb/10^6 ft^2/operation):								
Copper	32,7	16,4	18,4	9,2	16,4	8,2	24,6	12,3
Nickel	32,7	16,4	18,4	9,2	16,4	8,2	24,6	12,3
Chromium:								
Total	32,7	16,4	18,4	9,2	16,4	8,2	24,6	12,3
Cr^{+6}	3,3	1,6	1,8	9,2	1,6	0,82	2,4	1,2
Zinc	32,7	16,4	18,4	9,2	16,4	8,2	24,6	12,3
Cyanide:								
Total	32,7	16,4	18,4	9,2	16,4	8,2	24,6	12,3
Amenable	3,3	1,6	1,8	9,2	1,6	0,82	3,8	1,9
Fluoride	1308	654	738	369	646	323	984	492
Cadmium	19,2	9,6	8,8	4,4	9,8	4,9	14,8	7,4
Lead	32,7	16,4	[d]	[d]	[d]	[d]	[d]	[d]
Iron	65,4	32,7	36,8	18,4	32,8	16,4	49,2	24,6
Tin	65,4	32,7	36,8	18,4	32,8	16,4	49,2	24,6
Phosphorus	65,4	32,7	36,8	18,4	32,8	16,4	49,2	24,6
Total suspended solids	1308	654	738	369	646	323	984	492
pH	6,0-9,5	6,0-9,5	6,0-9,5	6,0-9,5	6,0-9,5	6,0-9,5	6,0-9,5	6,0-9,5

TABLE 4.3 U.S. EPA Best Practicable Control Technology Currently Available
Effluent Limitations[a] (Suspended Indefinitely[b]):
Subpart B[c]

Effluent characteristic	Effluent limits	
	Daily	30-d Ave
Pollutant (lb/10^6ft2/operation):		
Silver	3,3	1,6
Gold	3,3	1,6
Cyanide:		
Total	3,3	1,6
Amenable	32,7	16,4
Chromium:		
Total	32,7	16,4
Cr+6	3,3	1,6
Indium	3,3	1,6
Osmium	3,3	1,6
Palladium	3,3	1,6
Platinum	3,3	1,6
Rhodium	3,3	1,6
Ruthenium	3,3	1,6
Phosphorus	65,4	32,7
Total suspended solids	1308	654
pH	6,0-9,5	6,0-9,5

[a] Plants employing more than 11 persons, discharging more than 2,061 gal/h from metal finishing processes, or having a production rate greater than 52,7 ft2/h per employee.

[b] Although these regulations were suspended and are not in effect, they may be used by permit writers as guidance.

[c] Described in Table 4.1.

TABLE 4.4 U.S. EPA Best Practicable Control Technology Currently Available

Effluent Limitations[a] (Suspended Indefinitely[b]):
Subparts A, B, and D-F[c]

Effluent characteristic	Effluent limits					
	Subparts A and B		Subparts D and F		Subpart E	
	Daily max	30-d ave	Daily max	30-d ave	Daily max	30-d ave
Cyanide (lb/10^6ft2/ operation):						
Amenable	3,3	1,6	1,8	0,92	1,6	0,82
Total	32,7	16,4	18,4	9,2	16,4	8,2
Flow	(.....Equalize.....)					
pH	6,0-9,9	6,0-9,0	6,0-9,0	6,0-9,0	6,0-9,0	6,0-9,0

a Plants employing less than 11 persons, discharging less than 2,061 gal/h from metal finishing processes, or having a production rate less than 52,7 ft2/h per employee.

b Altnough these regulations were suspended and are not in effect, they may be used by permit writers as guidance.

c Described in Table 4.1

TABLE 4.5 U.S. EPA Pretreatment Standards for Existing Sources : Subparts A, B, and D-H[a]

Pollutant	Pretreatment standard (mg/l)	
	Daily max	4-d ave
Plants discharging less than 10 000 gal/d:		
Cyanide, amenable	5,0	2,7
Lead	0,6	0,4
Cadmium	1,2	0,7
Plants discharging more than 10 000 gal/d (Alternative 1[b]):		
Cyanide, total	1,9	1,0
Copper	4,5	2,7
Nickel	4,1	2,6
Chromium	7,0	4,0
Zinc	4,2	2,6
Lead	0,6	0,4
Cadmium	1,2	0,7
Silver[c]	1,2	0,7
All metals	10,5	6,8

[a] Described in Table 4.1

[b] Mass-based standards

[c] Applies only to Subpart B.

TABLE 4.6 U.S. EPA Pretreatment Standards for Existing Sources:[a] Alternative 1[b] - Subparts A, B, and D-HC[c]

Pollutant	Pretreatment standard (lb/10^6ft^2/operation)					
	Subparts		Subpart B		Subpart H	
	Daily max	4-d ave	Daily max	4-d ave	Daily max	4-d ave
Silver	(d)	(d)	9,6	5,9	(d)	(d)
Cyanide, total	15,2	8	15,2	8	13,7	18,2
Copper	36	21,5	36	21,5	82,1	49,4
Nickel	32,8	20,5	32,8	20,5	74,8	46,9
Chromium	55,9	32	55,9	32	127,6	73,1
Zinc	33,6	20,9	33,6	20,9	76,6	47,5
Lead	4,7	3,3	4,7	3,3	10,8	7,4
Cadmium	9,6	5,9	9,6	5,9	21,9	13,3
Total metals	84	54,7	84	54,7	191,5	124,7

[a] Plants discharging more than 10 000 gal/d

[b] Mass-based standards. Equivalent to and may apply in place of standards shown in Table 4.5 on agreement between source and receiving POTW.

[c] Described in Table 4.1

[d] Not applicable

TABLE 4.7 Pretreatment Stndards for Existing Sources: [a] Alternative 2[b] - Subparts A, B, and D-H[c]

Effluent characteristic	Pretreatment standard	
	Daily max	4-d ave
Pollutant (mg/l):		
Cyanide, total	1,9	1,0
Lead	0,6	0,4
Cadmium	1,2	0,7
Total suspended solids	20,0	13,4
pH	7,5-10,0	7,5-10,0

[a] Plants discharging more than 10 000 gal/d

[b] Simplified standards. An optional control program that may be selected by the source with concurrence of the control authority. Requires the absence of strong chelating agents, reduction of hexavalent chromium, and neutralization with CaO or $Ca(OH)_2$.

[c] Described in Table 4.1

4.2 Canadian Environmental Protection Agency

The Canadian EPA has issued guidelines (6, 17, 59, 60) to limit the discharge of deleterious substances in effluents from the Canadian metal finishing industry. These guidelines are a national baseline requirement of what practices will be considered by the Federal Government to meet the intent of the Fisheries Act, but it is not a specific Law, they are based on Best Practical Technology.

(a) In any day the total concentration of specific parameters may not exceed the values given in Table 4.8.

(b) The pH may not be outside the range 6,0 to 9,5 at any time.

(c) Concentrated residules containing emulsion cleaners, chlorinated hydrocarbons and effluent treatment sludges should not be deposited with the effluent.

(d) Concentrated spent processing solutions and residules other than in (c) should be treated to meet the objectives in (a).

The analysis of samples and the keeping of proper records is the responsibility of the firm.

A Code of Good Housekeeping Practice has been prepared to indicate methods and practices which should be followed to assist in meeting the requirements of the guidelines.

TABLE 4.8 Canadian Metal Plating Effluent Limits (mg/l)

Pollution	Limit
Total suspended matter	30
Cadmium	1,5
Chromium (total)	1,0
Copper	1,0
Lead	1,5
Zinc	2,0
Nickel	2,0
Cyanide (oxidizable)	0,1
Cyanide (total)	3,0

4.3 United Kingdom Department of the Environment

The British Department of the Environment has published a Technical Memorandum on Arisings, Treatment and Disposal (including a Code of Practice) for metal finishing wastes (61).

Conditions for discharge to public sewers and to rivers are specified by the water authorities. The conditions have regard to the absorbing capacity of the immediate environment taking into account, for example, dilution, removal in treatment processes and natural processes, effect on treatment processes, use of receiving water ; consequently the consent conditions vary widely. A survey of consent conditions for 31 companies discharging to public sewers is given in Table 4.9.

TABLE 4.9 Summary of Consent Conditions for 31 Metal Finishing Companies in the U.K.

Parameter	Range	Comments
pH	5-12	6-10 most common
Total Metals	3-30 mg/l	1 at 100 mg/l ; 30 mg/l most common
Total Soluble Metals	5-25 mg/l	1 at 100 mg/l ; 10 mg/l most common
Total Suspended Solids	200 - 3 000 mg/l	400 mg/l most common ; 1 at 3 000 mg/l ; 1 at 200 mg/l

4.4 Europe

A draft European Council Directive controlling the levels of toxic metals in sewage sludges applied to land has been recently introduced (62). Table 4.10 compares the European Economic Council (EEC) recommended and mandatory values with the British Department of the Environment's Advisory Guideline values.

TABLE 4.10 EEC and British Limits of Metals in Land-Applied Sludges (kg/ha/yr based on a 10 year average)

Element	EEC		DE
	Recommended	Mandatory	Guideline
Cd	0,10	0,15	0,17
Cu	10	12	9,33
Ni	2	3	2,33
Pb	10	15	33,33
Zn	25	30	18,66
As	0,35	-	0,33
Cr	10	-	33,33
Hg	0,40	-	0,07

4.5 Water Quality Criteria

The available world literature from 27 sources on existing water quality criteria have been summarised (63) for the 15 main uses of water.

Tables 4.11 and 4.12 summarises the levels in drinking water and river/dam water of chemicals of relevance to the metal finishing industry. Also included in the tables are the categories under which the contaminants fall.

Table 4.13 lists the South African Bureau of Standards limits (64) for metals in drinking water. The effluent discharge regulations for South Africa have been summarised in Chapter 1.

The toxocological properties of compounds associated with the metal finishing industry are given in Table 4.14.

TABLE 4.11 Selected Quality Criteria for Drinking Water (63)

Determinant	Unit	Min	Med	Max
Aesthetic/Physical				
Conductivity	mS/m	30	100	200
Hydrogen Sulphide	mg/l	0	0,05	0,3
Iron	mg/l	0,050	0,300	1,000
Oils and Grease	mg/l	0	0,200	0,500
pH	pH units	5,0	6,5-9,0	9,5
High Toxicity				
Antimony	µg/l	0,2	50	50
Cadmium	µg/l	1	10	50
Gold	µg/l		20	
Lead	µg/l	30	50	100
Moderate Toxicity				
Chromium	µg/l	30	50	500
Cyanide	µg/l	10	200	200
Fluoride	µg/l	700	1 500	2 400
Nickel	µg/l	30	50	1 000
Silver	µg/l	10	50	50
Tin	µg/l		50	
Low Toxicity				
Aluminium	mg/l	0,05	0,15	0,50
Cobalt	mg/l	0,05	1	5
Copper	mg/l	0,01	1	10
Non-Toxic				
Chloride	mg/l	100	250	1 000
Sodium	mg/l	100	270	1 000
Sulphate	mg/l	100	250	500
Zinc	mg/l	0,2	5,0	15,0

TABLE 4.12 Selected Quality Criteria for River/Dam Water (Protection of Aquatic Life) (63)

Determinant	Unit	Min	Med	Max
High Toxicity				
Cadmium	µg/l	0,1	3	30
Copper	µg/l	5	5	200
Cyanide	µg/l	5	5	5 000
Hydrogen sulphide	µg/l	2	2	300
Lead	µg/l	20	30	100
Silver	µg/l		10	
Moderate Toxicity				
Aluminium	µg/l	100	-	1 500
Chromium	µg/l	10	50	100
Fluoride	µg/l	1 500	1 500	1 500
Iron	µg/l	200	200	1 000
Nickel	µg/l	25	50	50
Zinc	µg/l	30	100	100
Low Toxicity				
Cobalt	mg/l		1	
Tin	mg/l		1	
Non-Toxic				
Chloride	mg/l	50		400
Sodium	mg/l		500	
Sulphate	mg/l		1 400	

TABLE 4.13 Limit Concentrations for Metals in Drinking Water (mg/l) (SABS 241)

Metal	Desirable	Permissible
Cd	0.05	0.05
Cr	0.05	0.05
Cu	1.0	1.5
Fe	0.3	0.7
Mn	0.1	0.4
Ni	N.S.	N.S.
Pb	0.05	0.10
Zn	5	15

N.S. not specified.

TABLE 4.14 Toxological Properties of Compounds Associated with Metal Finishing (63)

Aluminium	classically regarded as non-toxic beause it is insoluble at neutral pH values. It is potentially toxic because it can go into solution under acidic or basic conditions. Soluble aluminium has been implicated as a neurotoxin.
Cadmium	highly toxic and cumulative poison to higher life-forms.
Chromium	an essential element in human nutrition but toxic in high concentrations.
Copper	an essential element and only causes toxic symptoms in high concentrations. Algal species can become tolerant to copper.
Cyanide	more toxic to fish than humans. It is rapidly degraded in the environment by bacterial action, it is more toxic at low pH values than at high pH values. The free cyanide is more toxic than cyanide complexed to metallic elements (e.g. iron).
Fluoride	an element which helps prevent dental cares but it has chronic long term toxicity at concentrations only slightly above the beneficial level.
Gold	in a soluble form it is highly toxic.
Hydrogen Sulphide	although toxic it imparts an unpleasant taste/smell to water well below the toxic level.
Iron	an essential element, the limits are based on aesthetic not toxic considerations.

TABLE 4.14 (continued)

Lead	a highly toxic and cumulative poison which effects nerve tissues. Lead is more toxic at low calcium concentrations than at high calcium concentrations.
Nickel	thought to be essential for animal and plant life. It can be toxic to certain plants in concentrations exceeding 0,2 mg/l.
Silver	it is only moderately toxic to man, its chief toxicity is towards aquatic life.
Sulphate	non-toxic to animals and human except at very high concentration levels where it exerts a purgative effect.
Zinc	it is non-toxic to humans, water containing high zinc concentrations should be screened for the highly toxic element cadmium which is commonly found in association with zinc.

CHAPTER 5. SURVEY OF METAL FINISHING FIRMS IN SOUTH AFRICA

5.1 Survey of Municipalities Receiving Metal Finishing Effluent

A questionaire (Appendix 2) relating to water management and effluent treatment in the processing of :-

(i) Metals (metal plating, fabrication, machining and finishing)

(ii) Fermentation products (beer, sorghum beer, distilleries including wine distilleries and yeast processing industries)

(iii) Pharmaceutical products (pharmaceuticals and patent medicines)

was sent to 118 Municipalities in May 1982 (Table 5.1). The primary objective of the survey was to collate existing knowledge on water and effluent problems of the above industries and to formulate on a co-ordinated basis, the scope for improved effluent treatment, water management and disposal of effluents.

The information requested included the following:-

(a) Sewage Works

(i) description of the sewage works

(ii) the receiving body of the final effluent

(iii) the method of sludge disposal

(iv) the domestic and industrial flow to the sewage works

(v) the water and effluent tariffs

TABLE 5.1 Location of Metal Finishing, Fermentation and Pharmaceutical Firms

TOWNS	FERM FIRMS	PROBLEMS	MAJOR LOAD	PHARM FIRMS	PROBLEMS	MAJOR LOADS	METAL FIRMS	PROBLEMS	MAJOR LOAD
ALBERTON	2		YES	1			3		YES
AMANZIMTOTI	1		YES				1		
BARBERTON									
BEAUFORT WEST									
BEDFORDVIEW									
BELLVILLE									
BENONI							2		
BENONI (RF IELD)									
BETHLEHEM									
BLOEMFONTEIN	2						2		
BOKSBURG							16		YES
BOTHAVILLE									
BRACKENFELL									
BRAKPAN							2		
BRITS				2			12	YES	YES
BRONKHORSTSPRUIT									
BULFONTEIN									
CAPE TOWN							51		
ATHLONE	3			5			7		
CAPE FLATS				1			7		
CARLETONVILLE							5		
CERES									
DESPATCH									
DIV COUN CAPE									
ATLANTIS							1		
BORCHERDS							1		
DURBAN									
CENTRAL							6		
SOUTHERN	4	bypassed					7	YES	
NORTHERN							1		
EAST LONDON							5	SEA DISCHARGE	
EMPANGENI									
ERMELO									
ESHOWE									
ESTCOURT									
EVANDER									
GEORGE									
GERMISTON									
WATERVAL									
DEKEMA	2		YES	3			11		YES
RONDEBULT	1	YES	YES	1			31	YES	YES
GOODWOOD									
GREYTOWN									
HARTSWATER									
HEIDELBERG									
HEILBRON									
HENNEMAN									
HERMANUS									
HOWICK									
ISIPINGO	SEWAGE PROCESSED BY AMANZIMTOTI								

TABLE 5.1 (continued)

TOWNS	FERM FIRMS	PROBLEMS	MAJOR LOAD	PHARM FIRMS	PROBLEMS	MAJOR LOADS	METAL FIRMS	PROBLEMS	MAJOR LOAD
JAN KEMPTDORP									
JOHANNESBURG									
GOUDKOPPIES	3	YES	YES	1			26		YES
ALEXANDRA				1			8		
OLIFANTSVLEI	1						36		YES
KEMPTON PARK	1	YES	YES	10			5		YES
KIMBERELY									
HOMEVALE	1								
KIMBERLEY	1								
BEACONSFIELD									
KING WILLIAMSTOWN									
KLERKSDORP							1		YES
KNYSNA									
KROONSTAD	2								
KUILSRIVIER									
LYDENBURG									
MESSINA									
MEYERTON									
MIDDELBURG									
MILNERTON									
MONTAGU									
MOSSELBAAI									
NELSPRUIT	1	YES							
NEWCASTLE							2		
NEW GERMANY							10	YES	YES
NIGEL									
H BICKLEY	1						3	YES	YES
CF GRUNDLING									
MARIEVALE									
OUDTSHOORN	2								
PAARL	6		YES						
PAROW									
PARYS									
PHALABORWA									
PIETERMARITZBURGH	1			3			13		YES
PIETERSBURG									
PINETOWN	1			1			9		
PORT ELIZABETH	2			1			19	YES	YES
PORT SHEPSTONE									
POSTMASBURG									
POTCHEFSTROOM	1								
PRETORIA									
DASPOORT	2	YES					3		YES
BAVIAANSPOORT							1	YES	YES
ROODWAL				1			2	YES	
QUEENSBURG									
RANDBURG									
RICHARDS									
RIVERSDALE									
ROBERTSON									
ROODEPORT									
RUSTENBURG	1								

TABLE 5.1 (continued)

TOWNS	FERM FIRMS	PROBLEMS	MAJOR LOAD	PHARM FIRMS	PROBLEMS	MAJOR LOADS	METAL FIRMS	PROBLEMS	MAJOR LOAD
SANDTON									
SCOTTBURGH									
SOMERSET EAST									
SOMERSET WEST									
SPRINGS									
ANCOR	3						18	MINOR	
McCOMB							1	MINOR	
STANDERTON									
STELLENBOSCH	5	YES	YES						
STRAND									
TZANEEN									
UITENHAGE							3		YES
UMKOMAAS									
UPINGTON									
VEREENIGING									
VIRGINIA									
VREDENBURG									
VRYHEID	1	YES							
WELKOM									
THERONIA	2	YES	YES						
WITPAN									
WELLINGTON									
WESTONARIA									
WITBANK	1								
WITRIVIER									
WOLMARANS									
WORCESTER									
ZEERUST									
TOTAL	54			31			317		

(vi) a copy of the effluent by-laws and proposed changes

(vii) the number of Metal Finishing, Pharmaceutical and Fermentation Industries discharging effluent and whether they caused significant problems to the operation of the sewage works

(viii) an analysis of raw sewage and the final effluent

(b) Specific Metal Finishing Firms

(i) name of firm
(ii) nature of business
(iii) annual water consumption
(iv) annual effluent and sludge production
(v) effluent analysis
(vi) special requirements for discharge
(vii) description of effluent treatment plant
(viii) specific problems encountered due to the nature of the effluent.

5.2 Location of Metal Finishing, Fermentation and Pharmaceutical Firms

The location of Metal Finishing, Fermentation and Pharmaceutical firms is given in Table 5.1. The total number of metal finishing firms is 317 and they are mainly concentrated on the Reef (46%) (Boksburg, Germiston, Johannesburg and Springs), Cape Town (16%), the Durban area (Durban, Pinetown and New Germany) (10%) and in Port Elizabeth (6%). All the metal finishing effluent in East London is discharged directly to sea.

A total of 13 municipalities stated that metal finishing companies were a major source of heavy metals and 8 municipalities experienced problems because of the presence of heavy metals in the incoming sewage.

TABLE 5.2 Costs of Water and Effluent Treatment In South Africa (May 1982)

TOWNS	WATER COST c/kl	EFFTNT COST c/kl	COMMENTS
ALBERTON	23.68	15 MINIMUM TARIFF	
AMANZIMTOTI	29	15+3((S/10+1.5)+(OA/50+1.5))	
BARBERTON	30		
BENONI	25.9	5+(0.025*PV)+(0.04*SS)	
BLOEMFONTEIN	21	NO SPECIAL TRADE EFFLUENT TARIFF	
BOKSBURG	23.4	5.26	
BRAKPAN	37.6	13	
CAPE TOWN	35.3	TREATMENT 13.65 CONVEYANCE 8.19	
CARLETONVILLE	20	7.3	
DIV COUN CAPE	32	4+(COD/1000)*25	
DURBAN	20.4		
GERMISTON	24.474		
HEIDELBERG	31	10.0+(PV-60)/6	
HENNEMAN	9.17		
JOHANNESBURG	32.12	13.7+(.071*PV)/80	
KEMPTON PARK		6*0.08*(PV-50)	
KIMBERELY	22.57		
KLERKSDORP	27.8		
KROONSTAD	23		
KUILSRIVIER	31		
LYDENBURG	30		
MIDDELBURG	30	12	
MILNERTON	38		
NELSPRUIT	24		
NEWCASTLE	31.34	16	
NEW GERMANY			
NIGEL	30	7*(COD/600)	
OUDTSHOORN	25	14.17	
PAARL	31.8	5.87+7.26*(COD/1000)	
PARYS	21		
PIETERMARITZBURG		5.2+0.35*(PV-70)	
PINETOWN		4.4+(SS/10)+(OA/25)	
PORT ELIZABETH	27.5	11	
POTCHEFSTROOM	20	10.5	
PRETORIA	24	7+.047(PV-80) + 1.7(M-20)/PH	M = METALS IN MG/L IF GREATER THAN 20
RANDBURG	37		
RUSTENBURG	32.5	6 MIN	
SCOTTBURG	21		
SPRINGS	27.1	9.3+0.116(PV-80)	
STELLENBOSCH	33	.175PV	
UITENHAGE	19	10.06	
VEREENIGING	22	3.3+(OA-50)/91	
VREDENBURG	65		
WELKOM	34.9	7.27	
WESTONARIA	30		
WITBANK	16	5	
WORCESTER	20		
ZEERUST	11		

5.3 Cost of Water and Effluent Treatment

The cost of raw water and the effluent treatment tariff in different Municipalities is given in Table 5.2. The cost of water varied from 9,17 c/kl (Henneman) to 65 c/kl (Vredenburg/Saldanha) with a median cost of about 30 c/kl.

The effluent tariff generally consisted of a fixed cost which varied from 5 c/kl (Witbank) to 14,17 c/kl (Oudtshoorn) or else was dependant on conveyance (3,3 to 15 c/kl) and a permanganate value (PV) term.

Three municipalities used chemical oxygen demand (COD) in place of PV while 3 included a suspended solids factor.

Most municipalities had limits on the heavy metal concentration. Pretoria's tarrif included a charge for heavy metals if they exceeded 20 mg/l.

5.4 Industrial Effluent Contribution of Sewage Works

The average industrial and domestic inflows to sewage works are given in Table 5.3.

The sewage works with the greatest inflow of industrial effluent are Durban (Southern sewage works) - 42 Ml/day, Port Elizabeth - 25 Ml/day and Cape Town (Athlone) - 20 Ml/day. A total of 10 sewage works receive more than 40% of their inflow as industrial effluent.

The capacity of the Zeerust sewage works is obviously incorrect.

TABLE 5.3 Domestic and industrial flow to Sewage Works

TOWNS	TOTAL Ml/day	DOMESTIC Ml/day	COMMENTS
ALBERTON	24	22	TO GERMISTON DEKEMA
ALBERTON	8		TO GERMISTON WATERVAL
AMANZIMTOTI	12	10	
BARBERTON	2	2	
BENONI			
RYNFIELD	7	7	
BENONI	16	11	
BLOEMFONTEIN	40	39	
BOKSBURG	40	24	
BRAKPAN	8	7	
CAPE TOWN			
ATHLONE	80	60	
CAPE FLATS	88	7	
CARLETONVILLE	5	4	
DESPATCH	3	3	
DIV COUNCIL CAPE			
ATLANTIS	3	2	
BORCHERDS	13	10	
DURBAN			
SOUTHERN	106	64	
CENTRAL	69	61	
NORTHERN	26	24	
KWAMASHU-OLD	14	14	
KWAMASHU-NEW	13	13	
GERMISTON			
WATERVAL	20	17	
DEKEMA	41	24	
RONDEBULT	40	36	
GOODWOOD			TO MILNERTON AND CAPE TOWN (ATHLONE)
HEIDELBERG	84	80	
ISIPINGO			TO AMANZIMTOTI
JOHANNESBURG			
GOUDKOPPIES	145	132	
ALEXANDRA	167	153	
OLIFANTSVLEI	223	214	
KEMPTON PARK	55	36	
KIMBERELY			
HOMEVALE	8	?	
KIMBERELY	3	?	
BEACONSFIELD	4	?	
KLERKSDORP	16	12	

TABLE 5.3 (continued)

TOWNS	TOTAL Ml/day	DOMESTIC Ml/day	COMMENTS
KROONSTAD	8	7	
KUILSRIVIER	6	6	
LYDENBURG	2	2	
MIDDELBURG	8	8	
MILNERTON	12	12	
NELSPRUIT	5	3	
NEW CASTLE	6	4	
NEW GERMANY	3	2	
NIGEL			
H BICKLEY	4	2	
CF GRUNDLING	2	2	
MARIEVALE	1	1	
OUDTSHOORN	4	?	
PAARL	18	14	
PARYS	2	1	
PIETERMARITZBURG	40	34	
PORT ELIZABETH	60	35	
PRETORIA			
DASPOORT	76	68	
BAVIAANSPOORT	11	10	
ROODWAL	77	73	
QUEENSBURG	1	1	
RANDBURG	14	14	
RUSTENBURG	8	7	
SCOTTBURG	1	1	
SPRINGS			
ANCOR	27	22	
MCCOMB	9	6	
STELLENBOSCH	25	21	
UITENHAGE	12	7	
VEREENIGING	18	17	
VREDENBURG	1	1	
VRYHEID	4	1	
WELKOM			
THERONIA	22	7	
WITPAN	23	7	
WESTONARIA	8	8	
WITBANK	16	12	
WITRIVIER	1	1	
WORCESTER	11	6	
ZEERUST	127	120	
TOTAL	2 049	1 615	

TABLE 5.4 Sewage Works Description

TOWNS	PRIMARY SED	BIO FILTER	ACTIVATED SLUDGE	MATN PONDS	PRIMARY DIGN	SECONDARY DIGN	DRY BEDS	OTHER
AMANZIMTOTI	Y		Y		Y	Y		CENTRIFUGE
BARBERTON			Y	Y			Y	
BENONI	Y	Y			Y		Y	FILTRATION
RYNFIELD	Y	Y	Y	Y	Y		Y	DAF
BLOEMFONTEIN	Y	Y		Y	Y	Y	Y	
BOKSBURG	Y	Y		Y	Y	Y	Y	FILTRATION AND INCINERATION
BRAKPAN	Y	Y			Y	Y	Y	FILTRATION
BULTFONTEIN				Y				
CAPE TOWN								
ATHLONE	Y	Y		Y	Y	Y	Y	
CAPE FLATS	Y		Y	Y	Y		Y	
CARLETONVILLE	Y	Y		Y	Y		Y	
DESPATCH			Y					
DIV COUNCIL CAPE								
ATLANTIS			Y	Y			Y	
BORCHERDS			Y	Y			Y	CENTRIFUGE
DURBAN								
SOUTHERN	Y		Y		Y	Y		CENTRIFUGE
CENTRAL	Y							CENTRIFUGE AND INCINERATION
NORTHERN	Y		Y	Y	Y	Y		FILTRATION
KWAMASHU-OLD	Y	Y		Y	Y	Y	Y	
KWAMASHU-NEW	Y		Y	Y				CENTRIFUGE AND INCINERATION
EVANDER	Y	Y	Y	Y		Y	Y	FILTRATION
GERMISTON								
WATERVAL	Y		Y	Y	Y	Y		INCINERATION
DEKEMA	Y	Y			Y			INCINERATION
RONDEBULT	Y	Y	Y		Y			CENTRIFUGE AND INCINERATION
HARTSWATER				Y				
HEIDELBERG			Y					
HENNEMAN			Y				Y	
HERMANUS			Y					
HOWICK			Y				Y	
JOHANNESBURG								
GOUDKOPPIES	Y		Y					DAF AND BELT FILTER
KILPSPRUIT	Y	Y			Y	Y		
ALEXANDRA			Y					
NORTHERN	Y	Y	Y	Y	Y	Y	Y	DAF AND BELT FILTER
OLIFANTSVLEI	Y	Y	Y	Y	Y	Y	Y	DAF AND BELT FILTER
KEMPTON PARK	Y	Y	Y	Y	Y	Y	Y	
KIMBERELY								
HOMEVALE			Y	Y			Y	
KIMBERELY	Y	Y		Y	Y	Y	Y	
BEACONSFIELD	Y	Y			Y	Y	Y	

TABLE 5.4 (continued)

TOWNS	PRIMARY SED	BIO FILTER	ACTIVATED SLUDGE	MATN PONDS	PRIMARY DIGN	SECONDARY DIGN	DRY BEDS	OTHER
KLERKSDORP	Y	Y	Y			Y	Y	FILTRATION
KROONSTAD	Y	Y			Y	Y	Y	FILTRATION
KUILSRIVIER			Y	Y	Y		Y	
LYDENBURG		Y		Y			Y	FILTRATION
MIDDELBURG			Y	Y			Y	
MILNERTON	Y	Y		Y			Y	ZIMPRO SLUDGE CONDITIONING
NELSPRUIT	Y	Y			Y		Y	
NEWCASTLE	Y	Y		Y	Y		Y	
NEW GERMANY	Y		Y		Y			FILTRATION
NIGEL								
H BICKLEY	Y	Y			Y		Y	
CF GRUNDLING			Y				Y	
MARIEVALE	Y	Y			Y		Y	
OUDTSHOORN	Y	Y		Y	Y	Y	Y	
PAARL	Y	Y		Y	Y	Y	Y	
PARYS	Y	Y			Y	Y	Y	FILTRATION
PIETERMARITZBURGH	Y	Y	Y	Y	Y			
PORT ELIZABETH	Y		Y					CENTRIFUGE AND ZIMPRO
POTCHEFSTROOM	Y	Y	Y	Y	Y	Y	Y	
PRETORIA								
DASPOORT	Y	Y	Y		Y	Y	Y	CENTRIFUGE
BAVIAANSPOORT	Y		Y		Y			
ROODWAL	Y	Y		Y	Y	Y		
QUEENSBURG			Y				Y	
RUSTENBURG	Y	Y		Y	Y	Y	Y	
SCOTTBURG	Y		Y		Y	Y	Y	
SPRINGS								
ANCOR	Y	Y			Y	Y	Y	CENTRIFUGE
MCCOMB	Y	Y			Y	Y	Y	
STELLENBOSCH	Y	Y		Y	Y	Y	Y	
UITENHAGE	Y	Y		Y	Y	Y	Y	
VEREENIGING	Y	Y			Y			
VIRGINIA	Y	Y		Y	Y	Y	Y	
VREDENBURG			Y					
VRYHEID		Y						
WELKOM								
THERONIA	Y	Y		Y	Y		Y	CENTRIFUGE
WITPAN	Y	Y		Y	Y		Y	
WESTONARIA		Y		Y	Y	Y	Y	FILTRATION
WITBANK	Y	Y			Y		Y	
WITRIVIER			Y					
WORCESTER	Y	Y		Y	Y	Y	Y	
ZEERUST			Y					

5.5 Sewage Works Description

The description of the unit operation of the sewage works is given in Table 5.4.

Of the 13 municipalities (16 sewage works) which stated that metal finishing factories were a major load of heavy metals,

10 sewage works had biofilters,
10 sewage works had activated sludge plants,
5 sewage works had both biofilters and activated sludge plants,
7 sewage works had maturation ponds,
14 sewage works had primary/secondary digestion.

Of the 8 municipalities (10 sewage works) which stated that heavy metals from metal finishing factories were a problem,

4 sewage works had biofilters,
6 sewage works had activated sludge,
1 sewage works had both biofilters and activated sludge,
1 sewage works had maturation ponds,
7 sewage works had primary/secondary digestion.

5.6 Chemical Analysis of Sewage Works Influent and Effluent

The chemical analysis of the influent and effluent from the surveyed sewage works is given in Table 5.5.

The pH of the feed to the sewage works varied from 4,5 (Westonaria) to 7,9 (Vereeniging) while that of the effluent from the sewage works varied from 6,5 (Welkom - Witpan) to 9,2 (Cape Divisional Council - Atlantis).

A full chemical analysis was not carried out at all the sewage works, however, using the results available it was found that of the inflow to the sewage works :-

- the aluminium in Johannesburg and Boksburg was above 1 mg/l.

- cadmium levels at Rustenburg, Springs, Johannesburg, Nelspruit,

Cape Town and Boksburg were above 0,01 mg/l.

- Hexavalent chrome was above 0,2 mg/l at Uitenhage, Pretoria (Roowal and Baviaanspoort), Heidelberg, Johannesburg (Goudkoppies and Klipspruit), Boksburg and Cape Town (Athlone).

- Chrome III or total chrome was high in Pietermaritzburg (2 mg/l), Boksburg (1 mg/l) and Cape Town (Cape Flats) (1,67 mg/l).

- Cobalt was lower than 0,1 mg/l in Springs, Boksburg, Cape Town (Athlone).

Durban (Southern) and Boksburg had the highest hexavalent chrome in the effluent (0,197 mg/l and 0,2 mg/l respectively).

- Copper exceeded 0,1 mg/l at Amanzimtoti, Boksburg, Cape Town, Cape Divisional Council (Atlantis and Borcherds), Johannesburg (Goudkoppies, Klipspruit and Northern), Port Elizabeth and Uitenhage.

- Iron exceeded 1 mg/l at Boksburg, Cape Town, Cape Divisional Council, Johannesburg, Nigel and Uitenhage.

- Lead exceeded 0,1 mg/l at Amanzimtoti, Boksburg, Cape Town, Durban (Southern), Johannesburg (Goudkoppies and Klipspruit), Port Elizabeth and Uitenhage.

- Managanese exceeded 0,1 mg/l at Cape Town (Athlone), Johannesburg (Goudkoppies, Klipspruit), Parys, Port Elizabeth and Rustenburg.

- Nickel exceeded 0,1 mg/l at Boksburg, Atlantis, Borcherds, Johannesburg (Goudkoppies and Klipspruit), Pietermaritzburg, Port Elizabeth, Pretoria (Baviaanspoort, Rooiwal) and Springs.

- Sodium exceeded 150 mg/l at Cape Town (Athlone) Atlantis, Borcherds, Kempton Park and Nigel. Sodium was below 50 mg/l at Nelspruit.

- Zinc exceeded 1 mg/l at Amanzimtoti, Boksburg, Cape Town (Athlone), Atlantis, Borcherds, Johannesburg (Klipspruit, Alexandria and Northern).

TABLE 5.5 Chemical Analysis of Sewage Works Influent and Effluent
(All values except pH in mg/l)

Town		pH	Al	Cd	Cr6	Cr3	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl	CN	NO3	SO4	PO4	TDS	SETS	SUS	OA	BOD	COD
AMANZIMTOTI	In	6.6			0			.2		.5		0			2.7		117		0		24		7	426	85	785	1116
	Out	7.3			0			.1		.2		0			1.6		126		.2		18	648		174	22		202
BENONI	In	7.5															110				13.4		8.5		70		800
	Out																										120
BLOEMFONTEIN	In																					300	10		50		650
	Out																					300	0	5	5		50
BOKSBURG	In	7.6	1	1	1	1	1	1	2	1		1	120		2		150		0		10	850	8		65		800
	Out	7.6	.2	.2	.2	.2	.2	.2	2						.5		155		2		3	790	0		5		50
BRAKPAN	In	7.6																			12		8.5	19	45		688
	Out	7.6																	.2		14	740	0	12	7		65
CAPE TOWN																											
ATHLONE	In	7.4		.016	.24			.13	.21	3.1	.2	.1	.08	172		1	225			117	9.4	890	8	307	91	317	880
	Out	7.5		.011	.09			.009	.05	1	.05	.01	.07	164		.3	195		.42	91	6.3	750	0	31	26	42	181
CAPE FLATS	In	7.1		.009		1.67		.014	.393	4	.17	.14	.025	112		.77			.37		24.4	597	30.7	629	85		1128
	Out	7.2		.008		.01		.007	.018	.4	.03	.04	.018	123		.03	161		2.5		4.8	550	.1	12	14		63
CARLETONVILLE	In	7.0																			10						
	Out	6.7																			10.2			24	10.5		62
DIV COUNC CAPE																											
ATLANTIS	In	7.6		.1	.1				1	15			.1	199		3	249			129	48	982	18	494		457	1128
	Out	9.2								4				210			290		11.2	126	5	870	.1	12		3	55
BORCHERDS	In	7.2		.1		.2			.7	18			.3	165		4	194		0	112	40	856	11	380		477	1023
	Out	7.5								1				174			208		4.4	120	15	767	.1	16		20	73
DURBAN																											
SOUTHERN	In	7.2		.001	.184				.063		.127		.045			.316	91					906	7.9	242	71	284	799
	Out	6.9		.001	.197				.081		.075		.078			.337							1.3	146	66		37
CENTRAL	In	7.0		.001	.054				.066		.038		.071			.344	162					957	5.9	271	76	368	856
	Out	7.2			.08				.07		.04		.07			.34	159					771	.3	98	56	233	547
NORTHERN	In	7.2		.001	.017				.03		.026		.016			.078	57				16	784	9.8	383	47	197	580
	Out	7.5															57		6					39	6	4	58
KWAMASHU-OLD	In																						7.1	304	44	300	641
	Out																							14	5	4	33
KWAMASHU-NEW	In																						6.4	257	42	292	609
	Out																							14	5	4	33

TABLE 5.5 (continued)

Town		pH	Al	Cd	Cr6	Cr3	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl	CN	NO3	SO4	PO4	TDS	SETS	SUS	OA	BOD	COD
GERMISTON																											
WATERVAL	In																				19	720	9.6		79		1011
	Out																		8.5		4.6	583	0	16	9		55
DEKEMA	In																				23	748	10	425	71		930
	Out																		6.3		13	703	0	19	9		74
RONDEBULT	In																				16	1098	7.1	315	96		1232
	Out																		4.7		10	807	0	24	13		98
HEIDELBERG	In	7.2			1				1				148		.3				0		17	492	10	144	53		680
	Out	7.4			0				0				113		0				2.6		11	583	0	.6	6		44
JOHANNESBURG																											
GOUDKOPPIES	In	7.3	.77	.015	.26			.42	2.1	.1	.2	.23	96		14		83		0		3			240	55	210	740
	Out	7.5	.13	.008	.056			.16	.64	.014	.12	.18	91		.5		80		4.4	200		610		21	8	11	55
KLIPSPRUIT	In	6.8	3.7	.021	.68			.8	9.6	.12	1.1	.47	100		2.1		130		0		7.2			600	120	210	1300
	Out	7.3															120		68		65	600		78		39	220
ALEXANDRA	In	7.4	1.1	.024	.14			.24	1.2	.008	.028	.19	89		.78		77		0		3.9			160	43	120	530
	Out	7.4	1	.003	.048			.11	.98	.019	.087	.073	80		1.2		67		0		4.8	580		9	6	6	47
NORTHERN	In	7.4	1	.003	.048			.11	.98	.019	.087	.073	80		1.2		67		0		4.8			250	43	200	580
	Out	8.1	.24	0	.003			.12	.26	.003	.11	.043	84		1.2				6.9	1.5	4.9	530		11	5	6	41
OLIFANTSVLEI	In	7.4															7.6				3.6			190	48	200	570
	Out	7.8	.11	.001	.018			.011	.23	.041	.028	.19	83		.22		7.5		6.1	170	2.9	520		22	9	9	73
KEMPTON PARK	In	6.9	.8	.005	.002			3	1		.15	.2	150		.2	1	80	1	0	250	10		10		110		1100
	Out	8	.16	.005	0			0	0		.08	.14	150		.08	.47	80	1	2.1	190	8.7	600	.1	14	8		70
KIMBERLY																											
HONEYDALE	In	7.5															145						14		92		1180
	Out	8.4															245		.5			1202	0		5.4		70
KIMBERLY	In	7.6																					5		36		419
	Out	8.4																				1202	0		5.4		70
BEACONSFIELD	In	7.6																					7.5		46		504
	Out	7.7																	6.2				.2		7.2		45
KLERKSDORP	In																										
	Out	7.7									.1						110		.04			950	980	23	5.5	5.5	

TABLE 5.5 (continued)

Town		pH	Al	Cd	Cr6	Cr3	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl	CN	NO3	SO4	PO4	TDS	SETS	SUS	OA	BOD	COD
KROONSTAD	In																										
	Out	7.4																	4.8		9.4	550		10	9.2		60
KUILSRIVIER	In																						11		39		582
	Out																						.05		11		62
LYDENBURG	In	6.9																				364	2	25	40	192	488
	Out	8.1															48		5.2		5	280	.5	12	9	4	40
NELSPRUIT	In	7.3	.12	.03	0	.01	.004	.028	.42	.027	.956	.015	19.7		.076	.02	34.5		76	34	17	329	240	35	35		88
	Out	6.9	.11	.04	0	.008	.004	.034	.29	.018	.066	.012	20.3		.098	.03	37.8		66	66	20	280	96	20.2	15		10
NEWCASTLE	In	7.4		0		.36		0	.23						.54		54		4		78	426	9	70	46		120
	Out	8.1		0		.3		0	.12						.35		54		26		47	349	.5	9	9		48
NEW GERMANY	In	7.4																			8		21	76	36	41	172
	Out	7.0																	16		8			13	8	8	41
NIGEL																											
H BICKLEY	In	7.1		0	0				1				192		.3				0		6.4	1258	15	98	68		574
	Out	7.5		0	0				0				186		.2				16		6.4	1116	0	9.4	12		82
OF GRUNDLING	In	7.6		0	0				.1				141		.1				0		4.2	726	15	375	84		1080
	Out	7.2		0	0				0				109		.1				12		3.4	510	0	8	9		36
MARIEVALE	In	7.0		0	0				0				68		.1				0		2.8	491	7	201	18		610
	Out	7.2		0	0				0				61		.1				7.2		2.8	382	0	5	3		31
PARYS	In										.16																
	Out	7.1															124		1	7		1000	950	53	18	6.4	121
PIETERMARITZBURG	In	6.9	.1			2			.9			.5	66		.2				.02		12	374	45	189	38	220	60
	Out	7.0				2			9.6				43		.1				3.9		3	262		12	5	399	38
PORT ELIZABETH																											
INDUSTRIES	In	6.7				.8		.2		.6	.2	.1			2.6								12	808	123		1448
	Out	7.9				.2		.1		.1	.1	.1			.7				7.5					129	25		256
DOMESTIC	In	6.9				.4		.1		.2	.1	.1			1.3								9	493	59		794
	Out	7.5				.1		.1		.1	.1	.1			.2				6.8					27	10		101

TABLE 5.5 (continued)

Town		pH	Al	Cd	Cr6	Cr3	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl	CN	NO3	SO4	PO4	TDS	SETS	SUS	OA	BOD	COD
PRETORIA																											
BAVIAANSPOORT	In	7.7			.13			.08				.15			.42		76		2.4		33.9		9.6		54.2	369	815
	Out	7.9			.07			0				.03			.18		76		45.7		16.7	461	0	11	7.3	4.3	58
DASPOORT	In	7.4			.2	.35						0			.4		63		2.2		21		8		37	296	577
	Out	7.9			0	.07						0			.12		63		25.6	118	9.2	415	0	25	8.4	20	75
ROODWAL	In	7.2			5.4							.11			1.97		109				28		14.6		51	336	784
	Out	7.6			.05							.08			.19		109		49		28	618	0	14.3	8.6	8.6	74
RUSTENBURG	In	7.5	.3	.025	.14			.037	.23	.077	.109	.019	108.		.101	12	110		13.6	264	38	625	16	774	100		1157
	Out	7.1	.3	.025	.11			.024	.049	.066	.058	.016	102		.117	12	94		126	161	36	609	0	5	9		54
SCOTTBURGH	In	6.9																			8.5		14	302	16		623
	Out	6.8																	13.3		6.8	486		16	7		52
SPRINGS																											
ANCOR	In	7.6																					10		62		857
	Out	7.5		.02		.02	.11	.05	.3	.02		.3	100		.15		96		14.5	183	13	740	0	16	9.4		70
MCCOMB	In											.13											7		31		550
	Out	7.7		.03		.02	.03	.06	.59	.02		.13	85		.17		85		9.8	184	7	800	0	18	7.2		71
STELLENBOSCH	In	6.5															67		50		13		7.2		86		1057
	Out	7.4															70				15		0		13		98
UITENHAGE	In	7.3			.4		0	.1	1.7	.2	0	0	130	0	3		300	.01		230	30.4	800	8	100	54	380	740
	Out	7.7			.02		0	.1	.5	.02	0	0	145	0	.1		360	0	10	240	25.3	850	0	6	19	17	200
VEREENIGING	In	7.9															141		.1		26		10		82	520	975
	Out	8.0											113				123		22	260	25	894	0	15	11	26	83
WELKOM																											
THERONIA	In																126						9		25		723
	Out	6.9															145		6					.02	3.5		53
WITPAN	In																120						8.45		17		470
	Out	6.5															120		9					.02	2.8		32
WESTONARIA	In	4.5															43		0		8.6			152			469
	Out																44		0		10.4			18			6.6
WITBANK	In	7.6											82				63		.2		2.7	555	4	202	44		459
	Out	7.5											90				65		11		1.8	457	0	24	11		116
ZEERUST	In																										
	Out	8.0																									124

- Boron exceeded 1 mg/l at Rustenburg and Kempton Park.

- Chlorides exceeded 300 mg/l at Uitenhage.

- Cyanide was only determined at Uitenhage (0,01 mg/l) and Kempton Park (1 mg/l).

- Nitrates exceeded 50 mg/l at Nelspruit and Stellenbosch.

- Sulphates exceeded 150 mg/l at Johannesburg (Goudkoppies, Olifantsvlei), Kepmton Park, Rustenburg, Springs, Uitenhage and Vereeniging.

- Phosphates exceeded 20 mg/l at Amanzimtoti, Cape Town (Cape Flats), Atlantis, Borcherds, Germiston (Dekema), Newcastle, Pretoria (Baviaanspoort, Daspoort, Rooiwal), Rustenburg, Uitenhage and Vereeniging.

- TDS exceeded 1 000 mg/l at Germiston (Rondebult), Kimberely, Nige l (H. Bickley) and Parys.

The quality of the Sewage Works effluent was compared to the minimum, median and maximum values of international standards for toxic pollutants in river/dam water and in drinking water[63] (Tables 5.6 and 5.7).

Maximum values for river water are frequently exceeded. The maximum values for drinking water are exceeded by :-

Amamzintoti	lead
Boksburg	cadmium
Pietermaritzburg	chrome
Port Elizabeth	chrome, lead, nickel

5.7 South African Electroplating Chemical Consumption

An unsubstantiated estimate of the consumption plating chemicals in South Africa is given in Table 5.9. Not all the metal is plated on the product and the mass of chemicals which enter the effluent system would depend on the efficiency of the particular plating process.

5.8 Individual Metal Finishing Firms Effluent Characteristics

The characteristics of 131 individual metal finishing firm's effluent are given in Table 5.8.*

The total water usage of these firms was 8 800 Ml/year and they produced 6 880 Ml of effluent and 6 880 cubic metres of sludge. Two firms were exempted from the municipal bye laws, 34 firms had problems in treating their effluent to the required standards. A total of 92 firms had some type of inhouse effluent treatment system, 22 had no effluent treatment system (information as to the other 17 was not given). All the metal finishing firms in Johannesburg discharged directly to sewer. Special discharge conditions were imposed on 21 firms.

*In order to preserve confidentiality table 5.8 has been removed from this edition of the report.

TABLE 5.6 Comparison Between Sewage Works Effluent and River Water Standards (Table 4.12)

Towns	pH	Al	Cd	Cr^{6}	Cr^{3}	Co	Cu	Fe	Pb	Mn	Ni	Ne	Sn	Zn	B	Cl
Amanzimtoti							B		C					C		A
Benoni																
Bloemfontein																
Boksburg		A	C		C		C		C		C			C		A
Brakpan																
Cape Town																
Athlone			B		C		C		C		C			C		A
Cape Flats			B		A		B		B					A		A
Carletonville																
Div Council Cape																
Atlantis																
Borcherds																
Durban																
Southern			A				B		B		B			C		A
Central							B		B		B			C		A
Northern																
KwaMashu-Old																
KwaMashu-New																
Germiston																
Waterval																
Dekema																
Rondebult																
Heidelberg																

A - exceeds minimum value
B - exceeds median value
C - exceeds maximum value

TABLE 5.6 (continued)

Towns	pH	Al	Cd	Cr^{6}	Cr^{3}	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl
Johannesburg																
Goudkoppies		A	B		B		B				C			C		A
Klipspruit																A
Alexandra		A	B		A		B				C			C		A
Northern		A					B				A			C		
Olifantsvlei		A	A		A		B		C		C					
Kempton Park		A	B								C			A		A
Kimberely																
Homevale																A
Kimberely																
Beaconsfield																
Klerksdorp																A
Kroonstad																
Kullsriver																
Lydenburg																
Nelspruit		A	C				B							A		
Newcastle					C									C		A
New Germany																
Nigel																
H Bickley														C		
CF Grundling														C		
Marievale														C		

A - exceeds minimum value
B - exceeds median value
C - exceeds maximum value

TABLE 5.6 (continued)

Towns	pH	Al	Cd	Cr^{6}	Cr^{3}	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl
Parys																A
Pietermaritzburg					C									C		
Port Elizabeth																
Industries					C		B		C		C			C		
Domestic					C		B		C		C			C		
Pretoria																
Baviaanspoort					B		A				A			C		A
Daspoort					B		A							C		A
Roodwal					B						C			C		A
Rustenburg		A	B		C		B		B					C		A
Scottburgh																
Springs																
Ancor			B		A		B		A		C			C		A
McComb			C		A		B		A		C			C		A
Stellenbosch																
Ultenhage					A		B	A						C		A
Vereeniging																A
Welkom																
Theronia																A
Witpan																A
Westonaria																
Witbank																A
Zeerust																

A - exceeds minimum value
B - exceeds median value
C - exceeds maximum value

TABLE 5.7 Comparison between Sewage Works Effluent and Drinking Water Standards (Table 4.11)

Towns	pH	Al	Cd	Cr^{6}	Cr^{3}	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl
Amanzimtoti							B		C					A		A
Benoni																
Bloemfontein																
Boksburg		B	C		B	A	A					A		A		A
Brakpan																
Cape Town																
Athlone			B		B		A		B		B	A		A		A
Cape Flats							A		A			A				A
Carletonville																
Div Council Cape																
Atlantis												A				B
Borcherds												A				A
Durban																
Southern			A		B		A		B		B			A		A
Central					B		A		A		B			A		A
Northern																
KwaMashu-Old																
KwaMashu-New																
Germiston																
Waterval																
Dekema																
Rondebult																
Heidelberg												A				

A - exceeds minimum value
B - exceeds median value
C - exceeds maximum value

TABLE 5.7 (continued)

Towns	pH	Al	Cd	Cr^6	Cr^3	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl
Johannesburg																
Goudkoppies		A	A		B		A				B			A		
Klipspruit																A
Alexandra			A		B		A				B			B		
Northern		B					A				A			A		
Olifantsvlei		A					A		A		B			A		
Kempton Park		A	A								B	A				
Kimberely																
Homevale																A
Kimberely																
Beaconsfield																
Klerksdorp																A
Kroonstad																
Kuilsrivier																
Lydenburg																
Nelspruit		A	B				A									
Newcastle					B									A		
New Germany																
Nigel																
H Bickley												A				
CF Grundling												A				
Marievale												A				

A - exceeds minimum value
B - exceeds median value
C - exceeds maximum value

TABLE 5.7 (continued)

Towns	pH	Al	Cd	Cr^{6}	Cr^{3}	Co	Cu	Fe	Pb	Mn	Ni	Na	Sn	Zn	B	Cl
Parys																A
Pietermaritzburg					C											
Port Elizabeth																
Industries					B		A		C		B			A		
Domestic					B		A		C		C			A		
Pretoria																
Bevlaanspoort					B						A					
Daspoort					B											
Roolwal					B						B					A
Rustenburg		B	B		B		A		B							
Scottburgh																
Springs																
Ancor			B			A	A				B	A				
McComb			B				A				B					
Stellenbosch																
Uitenhage							A					A				B
Vereeniging												A				B
Welkom																
Theronia																B
Witpan																B
Westonaria																
Witbank																
Zeerust																

A - exceeds minimum value
B - exceeds median value
C - exceeds maximum value

In order to preserve confidentiality table 5.8 has been removed from this edition of the report.

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In order to preserve confidentiality table 5.0 has been removed from this edition of the report.

TABLE 5.9 Estimated Consumption of Plating Chemicals

Chemical	Form	Annual Consumption ton/yr
Cyanide	KCN ; NaCN	150 - 400
Chrome	Chromic acid	250
Cadmium	metal	50
Copper	metal	200
Nickel	metal	250
	$NiSO_4$; $NiCl_2$	200
Tin	metal	5 - 50

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

(i) Legislation exists to control and regulate the use of water and the discharge of effluents from the plating industry. Embodied in the legislation are provisions relating to specific water consumption, the installation of effluent treatment systems and exceptance limits for the chemical consumption (even if discharge into a municipal sewer system).

(ii) Technology is available to achieve the limits specified by the US EPA (Table 3.1). Sewage works with well operated primary and secondary biological treatment have removal rates for regulated metals (chromium, copper, nickel and zinc) of between 20 to 70%, BAT (best available technology economically achievable) is capable of removal levels of 97% or more.

(iii) Technology is available to enable certain plating solutions to be regenerated and recycled.

(iv) Metal finishing is a major point source of heavy metals.

(v) The presence of heavy metals in the influent to a few sewage works interfers with the operation of the sewage works.

(vi) At a number of sewage works the concentration of heavy metals in the effluent from the sewage works exceed the limits laid down in various international standards for both drinking water and river/dam water. This could have serious implications in the reuse of the water either as return flow or as reclaimed water.

(vii) The accumulation of heavy metals in the sewage sludge could limit management alternatives as to the disposal of the sludge.

(viii) The operation of the effluent treatment plants at metal finishing factories was very variable as indicated by the concentration of heavy metals in the effluent.

(ix) Conventional effluent treatment results in a significant increase in the total dissolved solids content of the effluent.

(x) The disposal of metal finishing sludges to land fill sites was not investigated.

6.2 Recommendations

6.2.1 Water Reduction

The first phase for an inhouse effluent treatment programme must be the reduction of water usage by the introduction of multiple counter current rise tanks preferably with water addition under conductivity control. The metal load from a conventional (precipitation) effluent treatment plant is directly proportional to the effluent volume hence reduction in water volume will also achieve a reduction in metal load. In the case of the installation of advanced effluent treatment/recycling processes, the reduction of effluent volume will lead to a reduction in both operating and capital costs.

6.2.2 Effluent Treatment

Conventional (precipitation) treatment is capable of achieving relatively low concentrations of heavy metals. The system is unsuitable if there are chelating or complexing agents present. In addition the salt load of the effluent is increased significantly. Recent overseas research has concentrated on resource recycling in preference to pollution abatement. This approach is suitable for dedicated plating lines but not for diverse plating operation which take place in jobbing shops. A number of alternative effluent treatment systems have been installed overseas with varying degress of success. Encouragement

must be given to the implementation of inovative technology to recycle metals and water and eliminate the discharge of effluents to sewer.

6.2.3 Future Research

Future research should concentrate on reducing or eliminating the discharge of heavy metal effluents. At the same time attention should be paid to the reduction in inorganic salt load. The final objective should be the isolation of metal finishing firms from the sewage treatment system by the application of closed loop recycling within the factory. The treatment processes that should be investigated are :

(i) electro-chemical
(ii) membrane
(iii) electro-membrane

Local research should concentrate on the isolation of metal finishing firms from the sewage treatment system by closed loop recycling within the factory.

6.2.4 Technology Transfer

The metal finishing industry is highly fragmented and consists of a large number of facilities. Consideration should be given not only to demonstrating existing and inovative technology to the industry but also in the up grading of existing facilities.

6.2.5 Ultimate Sludge Disposal

Greater provision of suitable sites should be made for the controlled dumping of potentially toxic sludges from the metal finishing industry. Monitoring programmes should be implemented in order to assess the effects of heavy metals in the agricultural use of sewage sludge and the effect of heavy metals in aqueous disposal of treated sewage.

APPENDIX 1 Some Chemicals Used in the Metal-Finishing Industry (19)

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products[1]
Aluminum potassium sulphate	X		MS,DS
Aluminum silicate	X		MS,DS
Ammonium acetate	X		DS,NH_3
Ammonium bifluoride	X		MS,DS,NH_3
Ammonium chloride	X		DS,NH_3
Ammonium citrate	X		DS,NH_3,O
Ammonium hydroxide	X		DS,NH_3
Ammonium molybdate	X		MS,DS,NH_3
Ammonium nitrate	X		DS,NH_3
Ammonium sulphate	X		MS,DS,NH_3
Anisic aldehyde	X		O
Antimony potassium tartrate	X		MS,DS,O
Barium carbonate	X		MS
Barium sulphate	X		MS
Benzene	X		O
Boric acid	X		DS
Cadmium cyanide		X	MS,DS
Cadmium sulphate	X		MS,DS
Calcium nitrate	X		DS
Chromic acid		X	MS,DS
Citric acid	X		DS,O
Cobalt carbonate	X		MS
Cobalt sulphate	X		MS,DS
Cupric sulphate	X		MS,DS

[1]MS = metal sludge; NH_3 = ammonia; DS = dissolved solids; O = organic matter

APPENDIX 1 (continued)

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products[1]
Diammonium phosphate	X		MS, DS, NH_3
Ferric nitrate	X		MS, DS
Fluoboric acid	X		MS, DS
Formaldehyde	X		O
Glue	X		O
Glycerine	X		O
Hydrazine sulphate	X		DS
Hydrochloric acid	X		DS
Hydrofluosilicic	X		MS, DS
Hydrogen peroxide	X		
Hydroxyacetic acid	X		DS, O
Hypophosphorus acid	X		MS, DS
Indium sulphate	X		MS, DS
Iron oxide	X		MS
Isopropanol	X		O
Lard oil	X		O
Lead fluoborate	X		MS, DS
Lead oxide	X		MS
Lime (calcium hydroxide)	X		MS

[1]MS = metal sludge; NH_3 = ammonia; DS = dissolved solids; O = organic matter

APPENDIX 1 (continued)

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products[1]
Magnesium sulphate	X		MS,DS
Manganese carbonate	X		MS
Manganese sulphate	X		MS,DS
Methanol	X		O
Monoammonium phosphate	X		MS,DS,NH_3
Nickel carbonate	X		MS
Nickel chloride	X		MS,DS
Nickel sulphate	X		MS,DS
Nickel sulfamate	X		MS,DS
Nitric acid	X		DS
Oxalic acid	X		MS,DS
Phosphorus acid	X		MS,DS
Potassium bromate	X		DS
Potassium citrate	X		DS,O
Potassium chloride	X		DS
Potassium copper cyanide		X	MS,DS
Potassium cyanide		X	MS,DS
Potassium ferricyanide		X	MS,DS
Potassium hydroxide	X		DS
Potassium phosphate	X		MS,DS
Potassium stannate	X		MS,DS
Potassium thiocyanate	X		DS

[1]MS = metal sludge; NH_3 = ammonia; DS = dissolved solids; O = organic matter

APPENDIX 1 (continued)

Chemical	p adjustment required	Cyanide or chromium treatment required	Waste products[1]
Sodium acid pyrophosphate	X		MS,DS
Soda ash (sodium carbonate)	X		DS
Sodium bicarbonate	X		DS
Sodium bisulfite	X		DS
Sodium bifluoride	X		MS,DS
Sodium citrate	X		DS,O
Sodium copper cyanide		X	MS,DS
Sodium cyanide		X	DS
Sodium dichromate		X	MS,DS
Sodium fluooborate	X		MS,DS
Sodium gluconate			
Sodium hexametaphosphate	X		MS,DS
Sodium hypophosphite	X		MS,DS
Sodium hydrosulfite	X		DS
Sodium hydroxide (caustic soda)	X		DS
Sodium metasilicate	X		MS,DS
Sodium molybdate	X		Ms,DS
Sodium nitrate	X		DS
Sodium orthosilicate	X		MS,DS
Sodium polysulfide	X		MS,DS
Sodium stannate	X		MS,DS
Sodium sulphate	X		DS
Sodium sulfide	X		MS,DS
Sodium sulfite	X		DS
Sodium tripolyphosphate	X		MS,DS
Stannous fluoborate	X		MS,DS
Stannous sulphate	X		MS,DS

[1]MS = metal sludge; NH_3 = ammonia; DS = dissolved solids; O = organic matter

APPENDIX 1 (continued)

Chemical	pH adjustment required	Cyanide or chromium treatment required	Waste products[1]
Stearic acid	X		O
Sulfamic acid	X		DS
Sulfur (liquid)	X		MS
Sulfuric acid	X		MS,DS
Tallow glyceride	X		O
Tartaric acid	X		O
Tetrapotassium pyrophosphate	X		MS,DS
Tetrasodium pyrophosphate	X		MS,DS
Toluene	X		O
Trichlorethylene	X		O
Trichloroethane	X		O
Trisodium phosphate	X		MS,DS
Xylene	X		O
Zinc chloride	X		MS,DS
Zinc cyanide		X	MS,DS

[1]MS = metal sludge; NH_3 = ammonia; DS = dissolved solids; O = organic matter

APPENDIX 2.

Dear Sir,

NATIONAL SURVEY INTO WATER MANAGERMENT AND EFFLUENT TREATMENT

The Pollution Research Group of the University of Natal, Durban is undertaking an investigation into the water management and effluent treatment in the processing of :

(i) Metals (metal plating, fabrication, machining and finishing).
(ii) Fermentation Products (beer, sorghum beer, distilleries including wine distilleries and yeast processing industries).
(iii) Pharmaceutic Products (pharmaceuticals and patent medicines).

The investigation/survey is being undertaken for the Water Research Commission in close cooperation with the Industries, the Department of Environment Affairs and Local Authorities to identify problems and areas where improvements can be made.

The primary objective of the project is to collate existing knowledge on water and effluent problems of the above industries and to formulate, on a coordinated basis, the scope for improved effluent treatment, water management and disposal of effluents.

The second objective of the project is to make recommendations to the Water Research Commission so that they can initiate, on a priority basis, research and development programmes for the solution of the identified problems.

It would be appreciated, therefore, if you would complete the attached questionnaire with reference to industries (i) to (iii), which discharge into the municipal sewers. If none of the above industries discharge into the minicipal sewer please fill in the name of the municipality and return the questionnaire.

Please be assured that the information will be treated as confidential and will not be published in any way which would make it possible to identify an individual company. The information which we are collecting will be used by the Water Research Commission to plan future research.

This is in the National interest and I am sure we can look forward to your cooperation and help.

APPENDIX 3.

CONFIDENTIAL QUESTIONNAIRE

METAL FINISHING FIRMS DISCHARGING EFFLUENT TO SEWER

(Information supplied is solely for use by the Water Research Commission to assess the need for future research in the Metal Finishing Industry and will not be disclosed to any other party.)

Please fill in a separate form for each firm.

1. Name of firm : .....

2. Address of firm : .....
.....

3. Nature of Business : .....
.....

4. Person responsible for effluent control : .....
.....

5. Annual water consumption : .....

6. Annual volume of effluent produced : .....

7. Volume or mass of sludges produced : .....

CONFIDENTIAL

8. Typical Analysis of Effluent

pH		_____
Aluminium	Al	_____
Cadmium	Cd	_____
Chrome (hexavalent)	Cr^{VI}	_____
Chrome (trivalent)	Cr^{III}	_____
Cobalt	Co	_____
Copper	Cu	_____
Iron	Fe	_____
Lead	Pb	_____
Manganese	Mn	_____
Nickel	Ni	_____
Sodium	Na	_____
Tin	Sn	_____
Zinc	Zn	_____
Boron	B	_____
Chloride	Cl^-	_____
Cyanide	CN^-	_____
Nitrate	NO_3^-	_____
Sulphate	$SO_4^=$	_____
Phosphate	$PO_4^=$	_____
Total Dissolved Solids		_____
Oils Fats and Greases		_____

9. Does the firm have exemption from the bye-laws? If yes, please specify :

.....

.....

.....

10. Are problems encountered in treating the effluent? If yes, please specify :

.....

.....

.....

CONFIDENTIAL

11. Does the firm have its own effluent treatment system? If yes, name unit operations or sketch a flow diagram :

.....

.....

.....

12. Are any special conditions required for discharge (e.g. balancing tanks, analysis prior to discharge) :

.....

.....

.....

.....

CONFIDENTIAL QUESTIONNAIRE

SURVEY ON METAL FINISHING, FERMENTATION PRODUCTS AND PHARMACEUTICAL PRODUCTS

(Information supplied is solely for use by the Water Research Commission to assess the need for future research in these industries and will not be disclosed to any other party.)

Please fill in a separate form for each sewage works.

1. Name of Municipality : .....

(Return the questionnaire if none of the above industries discharge effluent into the municipal sewers.)

2. Sewerage Works

(a) Type of works?

Primary sedimentation	___
Biological filter	___
Activated sludge	___
Maturation ponds	___
Primary digestion	___
Secondary digestion	___
Drying beds	___
Filtration	___
Centrifuge	___
Incineration	___
Other (specify)	

(b) The final effluent is discharged into : .....
.....
.....
The sludge is disposed by : .....
.....
.....

(c) Total flow to the sewage works : .....

CONFIDENTIAL

(d) Total flow of domestic sewage : .....

(e) Water Tariff : .....

(f) Effluent and treatment tariff : .....

(g) Please attach a copy of the effluent bye-laws and specify if any changes to the bye-laws are envisaged.

3. Heavy Metals

(a) Number of firms discharging metal finishing effluents : .....

(b) Have any problems been encountered because of the presence of heavy metals in the incoming sewage, if yes, please specify?

.....
.....
.....
.....

(c) Is metal finishing a major source of heavy metals in the incoming sewage?

.....
.....
.....
.....

CONFIDENTIAL

(d) Analysis of Sewage Effluent

		Raw Sewage	Final Effluent
pH			
Aluminium	Al		
Cadmium	Cd		
Chrome (hexavalent)	Cr^{vi}		
Chrome (trivalent)	Cr^{iii}		
Cobalt	Co		
Copper	Cu		
Iron	Fe		
Lead	Pb		
Manganese	Mn		
Nickel	Ni		
Sodium	Na		
Tin	Sn		
Zinc	Zn		
Boron	B		
Chloride	Cl^-		
Cyanide	CN^-		
Nitrate	NO_3^-		
Sulphate	$SO_4^=$		
Phosphate	$PO_4^=$		

(d) Analysis of Sewage (continued)

Total dissolved solids	
Settleable solids	
Suspended solids	
Oxygen absorbed	
Biological Oxygen Demand	
Chemical Oxygen Demand	

4. Fermentation Products

(a) Number of fermentation firms discharging effluent to the sewers? :

.....

CONFIDENTIAL

(b) Have any problems been encountered because of the presence of fermentation products in the incoming sewage? If yes, please specify :

.....
.....
.....
.....
.....

(c) Are effluents from fermentation products a major load in the incoming sewage ?

.....
.....
.....
.....

5. Pharmaceutical Products

(a) Number of pharmaceutical firms discharging effluent to the sewer ?

.....

(b) Have any problems been encountered because of the presence of pharmaceutical products in the incoming sewage? If yes, please specify.

.....
.....
.....
.....
.....

(c) Are effluents from pharmaceutical products a major load in the incoming sewage?

.....
.....
.....
.....

REFERENCES

1. Kriel, J.P., "Planning and Progress in the Development of the Water Resources of South Africa with Special Reference to South Western Cape", Congress of the South African Association for the Advancement of Science, Stellenbosch, (1975).

2. Republic of South Africa, "Report of the Commission Enquiring into Water Matters", R.P. 34/1970, (1970).

3. Republic of South Africa, "Water Amendment Act, 1984".

4. Best H.J., "The Practice of Control of Industrial Water Usage and Water Pollution within the Framework of THE WATER AMENDMENT ACT, 1984", Water Sewage Effluent, 18, pp. 5-11, Sept (1984).

5. Zunkel, C.F., "Current Trends in South Africa Regarding Effluent Discharge and Legislation", Water Sewage and Effluent, pp. 7-10, (1981).

6. Canadian Environmental Protection Service, "Review of the Canadian Metal Finishing Industry - Consumption of Raw Materials and Options for Water Pollution Control", Report EPS 3-WP-75-2, (1975).

7. Funke, J.W. and Coombs, P., "Water and Effluent Management in the Electroplating and Anodising Industry", CSIR, National Institute for Water Research, Technical Guide K29, Pretoria, South Africa (1973).

8. Canning, "The Canning Handbook on Electroplating", E. Canning Ltd, ISN 0 419 10950 1, Birmingham (1978).

9. United States of America Environmental Protection Agency, "Summary Report. Control and Treatment Technology for the Metal Finishing Industry. In-Plant Changes", US EPA 625/8-82-008, (1982).

10. United States of America Environmental Protection Agency, "Waste Treatment. Upgrading Metal Finishing Facilities to Reduce Pollution", US EPA 625/3-73-002, Vol 2, (1973).

11. WHO, "Rapid Assessment of Sources of Air, Water and Land Pollution", WHO Off Set Publication No 62, ISBN 92 4 170062 9, Geneva, (1982).

12. United States of America Environmental Protection Agency, "Development Document for Proposed Existing Source Pretreatment Standards for the Electroplating Point Source Category", US EPA 440/1-78-085, Feb (1978).

13. Ward, R.C., "Aluminium Anodising Wastewater Treatment and Reuse", Proc. 36th Industrial Waste Conference, pp. 540-548, Purdue, (1981).

14. United States of America Environmental Protection Agency, "Environmental Regulations and Technology. The Electroplating Industry", US EPA 625/10-80-001, (1980).

15. United States of America Environmental Protection Agency, "Effluent Limitation Guidance for the Refuse Act Programme, Metal Finishing Industry", US EPA, Sept (1972).

16. "Normal fur Abwasserreinigungsverfahrn", 2. erweiterte und uerarbeitete Auflage, Sonderdruck der Landeragrbeitsgemeinschaft Wasser, LAWA, (1970).

17. Canadian Environmental Protection Service, "Waste Water and Sludge Control in the Canadian Metal Finishing Industry", EPS 3-WP-76-10, (1976).

18. Brohan, H.K., "Electroplating Engineering Handbook", Reinhold Publishing Co., N.Y., (1955).

19. United States of America Environmental Protection Agency, "In-Process Pollution Abatement. Upgrading Metal Finishing Facilities to Reduce Pollution", US EPA 625/3-73-002, Vol. 1, (1973).

20. R. Weiner, Die Abwasser der Galvanotechnik und Metallindustrie, 4th edition, Eugen G. Leuze Verlag, (1973).

21. United States of America Environmental Protection Agency, "Environmental Pollution Control Alternatives : Centralised Waste Treatment Alternatives for the Electroplating Industry", US EPA 625/5-81-017, June (1981).

22. Habashi, F., "Principals of Extractive Metallurgy, Vol. 2-Hydrometallurgy", Gordan and Breacn, New York (1972).

23. McKavenay, J.P., Fassinger, W.P. and Strivers, D.A., "Removal of Heavy Metals from Water and Brine Using Silicone Alloys", Sci. and Tec., 6(13) pp. 1109, (1972).

24. United States of America Environmental Protection Agency, "Metallic Recovery from Waste Water Utilizing Cementation", US EPA 670/2-74-008, (1974).

25. United States of America Environmental Protection Agency, "Summary Report : Control and Treatment Technology for the Metal Finishing Industry - Sulfide Precipitation", US EPA 625/8-80-003, April (1980).

26. United States of America Environmental Protection Agency, "Waste Water Treatment and Reuse in a Metal Finishing Job Shop", US EPA Report 670/2-74-042, (1974).

27. United States Patent No. 2, 725, 314.

28. United States of America Environmental Protection Agency, "Assessment of Emergency Technologies for Metal Finishing Pollution Control : Three Case Studies", US EPA-600/2-81-153, August (1981).

29. United States of America Environmental Protection Agency, "Summary Report : Control Technology for the Metal Finishing Industry-Evaporators", US EPA 625/8-79-002, June (1979).

30. Crampton, P. and Wilmoth R., "Reverse Osmosis in the Metal Finishing Industry", Metal Finishing, 80 (3), pp. 21-27, (1982)

31. United States of America Environmental Protection Agency, "Treatment of Electroplating Wastes by Reverse Osmosis", US EPA 600/2-76-261, Sept (1976).

32. Larson, R.E., Petersen, R.J. and Cadotte, J.E., "The FT-30 Reverse Osmosis Membrane Three Years Experience in a Variety of Desalting Applications", Tenth Conference of Water Supply Improvement Association, Honolulu, Hawaii, July 25-29 (1982).

33. Cartwright, P.S., "What's New with Reverse Osmosis", American Electroplaters Society, 70 (C - 2), pp. 1-10, (1983).

34. United States of America Environmental Protection Agency, "Evaluation of Reverse Osmosis Membranes for Treatment of Electroplating Rinse Water", US EPA-600/2-80-084, (1980).

35. Mir, L., Eykamp, W. and Goldsmith R.L., "Current and Developing Applications for Ultrafiltration", Ind. Wat. Eng., 14, pp. 14-19, (1977).

36. Bhattacharyya, D., Jumawan, A.B. and Grieves, R.B., "Charged Membrane Ultrafiltration of Heavy Metals from Non-ferrous Metal", J. Wat. Poll. Cont. Fed., 51 (1) pp. 176-186, (1979).

37. Bhattacharyya, D., Schaaf, D.P. and Grieves, R.B., "Charged Membrane Ultrafiltration of Heavy Metal Salts: Application to Metal Recovery and Water Reuse", Canadian J. Chem Eng. 54, pp. 185-189, June (1976).

38. Shapiro, N.I., Liu, H., Baranski, J. and Kurzweg, D., "Removal of Heavy Metals and Suspended Solids from Battery Waste Water: Application of Hydroperm Cross-Flow Microfiltration", US EPA-600/S2-81-147, Sept (1981).

39. Liu, H.L. and Blacklidge, J., "Cross Flow Filtration Technology for Metal Finishers", Fourth Conference on Advanced Pollution Control for the Metal Finishing Industry, US EPA -600/9-82-002, December (1982).

40. Tulin, M.P., "Cross Flow Filtration", Paper presented at Fine Particle Society Fall Meeting, University of Maryland, Sept 16-18 (1980).

41. Anon, "Getting the Metal out of Spent Plating Baths", Chemical Engineering, pp. 22-24, May 16 (1983).

42. United States of America Environmental Protection Agency, "Investigation of Treating Electroplaters Cyanide Waste by Electrodialysis", US EPA-R2-73-287, (1973).

43. United States of America Environmental Agency, "Nickel Recovery from Electroplating Rinse Water by Electrodialysis", US EPA PB 81-227209, Oct (1981).

44. Basta, N., "Total Metals Recycle is Metal Finishing Goal", Chem Eng, pp. 16-19, 8 August (1983).

45. Murakami, H. and Igarashi, N., "PBIL Tubular Reverse Osmosis. Applications as Low-Energy Concentrators", I&EC Product Research and Development, 20 (3), pp. 501-508, (1981).

46. Bhattacharyya, D and Cheng, C.S., "Low Pressure Membrane Separation Process to Remove Heavy Metal Complexes", U.S. O.W.R.T., PB 82 224619, USA, Sept (1981).

47. Altmayer, F., "Introducing the COPS - One Step Regeneration and Purification of Chromic Pickling/Stripping Solutions", Plating and Surface Finishing, pp. 20-24, March (1983).

48. Smith, K.L., Babcock, W.C., Baker, R.W. and Conrod, M.G., "Coupled Transport Membranes for Removal of Chromium from Electroplating Rinse Solutions", in Chemistry in Water Reuse (Ed Cooper, W.J.) 1, pp. 311-324, (1981).

49. United States of America Environmental Protection Agency, "Coupled Transport Systems for Control of Heavy Metal Pollutants", US EPA 600/2-79-181, August (1979).

50. Kawashimat et al, "Treatment of Wastewater Containing Heavy Metal Ions Using Activated Charcoal", Mitzushou Gijutsu (Japan) 14 (4), pp. 379, (1972).

51. Huang, C.P. and Wu, M.M., "The Removal of Chrome (vi) from Dilute Aqueous Solutions by Activated Carbon", Water Research 11 (8), pp. 673-679, (1977).

52. Huang, C.P. and Bowers, A.R., "Activated Carbon Process for Treatment of Wastewaters Containing Hexavalent Chrome", US EPA 600/2-79-130, (1979).

53. Waltz, W.H., "Ion Exchange for Recovery of Precious Metals", Plating and Surface Finishing, 69, pp. 56-59, April (1982).

54. United States of America Environmental Protection Agency, "Control and Treatment Technology for the Metal Finishing Industry - Ion Exchange", US EPA 625/8-81-007, June (1981).

55. Horelick, P., "Recovery and Electrochemical Technology", Fourth Conference on Advanced Pollution Control for the Metal Finishing Industry, US EPA 600/9-82-002, pp. 67-69, (1982).

56. United States of America Environmental Protection Agency, "Environmental Pollution Control Alternatives : Sludge Handling, Dewatering, and Disposing Alternatives for the Metal Finishing Industry", US EPA 625/5-82-018, October (1982).

57. United States of America Environmental Protection Agency, "Environmental Regulations and Technology, The Electroplating Industry", US EPA 625/10-80-001, (1980).

58. United States of America Environmental Protection Agency, "Electroplating and Metal Finishing Point Source Categories ; Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards", US Federal Register, 47, (169), 31 August (1982).

59. Canadian Environmental Protection Service, "Metal Finishing Liquid Effluent Guidelines", Report EPS 1-WP-77-5, (1977).

60. Canadian Environmental Protection Service, "Waste Handling, Disposal and Recovery in the Metal Finishing Industry", Report EPS 3-WP-77-3, (1977).

61. Department of the Environmental, "Metal Finishing Wastes - A Technical Memorandum on Arisings, Treatment and Disposal Including a Code of Practice", Waste Management Paper No. 11, ISBN 0 11 751122 6, Her Majesty's Stationery Office, London, (1983).

62. Anon, "Tight Controls Proposed by EEC for Land Application of Sewage Sludge", Water World, pp. 27-29, Jan (1983).

63. Kempster, P.L., Hattingh, W.H.J. and Van Vliet, H.R., "Summarised Water Quality Criteria", Department of Environmental Affairs Technical Report TR108, ISBN 0 621 07110 2, Pretoria, (1980).

64. South African Bureau of Standards, "Specification for Water for Domestic Supplies", SABS 241, Pretoria, (1971).