in industry', *Prog. Water Technol.*, 1975, 7, 905
8 Ministry of Housing and Local Government, 'Taken for granted', *London: HMSO*, 1969, 38
9 Ministry of Housing and Local Government, 'Standards of effluent to rivers with particular reference to industrial effluents', *London: HMSO*, 1968
10 Mattock, G., 'Developing patterns of effluent treatment and recovery practices in the metal finishing industry', Paper presented to SCI international conference, Amsterdam, May 1974
11 'Development document for effluent limitation guidelines for the significant organic products segment of organic chemical manufacturing', *USA: EPA*, November, 1975, 440/1-75/045
12 Hackman, E., & Ellsworth, 'Toxic organic chemicals – destruction and waste treatment', *New Jersey: Noyes Data* 1978, 148
13 'Development document for effluent limitations guidelines for pesticide chemicals manufacturing', *USA: EPA*, November, 1976, 440/1-75/060d
14 Agg, A. R., 'Marine pollution and marine waste disposal', *Prog. Water Technol. Supplement*, 1975, 75
15 Chalmers, R. K., & Jenkins, S. H., 'A feasibility study of the control of pollution from industrial waste waters discharged into the lagoon of Venice', *Water Pollut. Control*, 1976, 75, 176
16 Reynolds, L. F., 'The disposal of waste water from the chemical industry', Proceedings of 3rd PHE Conference, Loughborough University, January, 1970, 65
17 Toogood, S. J., & Hobson, J. A., 'The determination of safe limits for the discharge of volatile materials to sewers', *Stevenage: Water Research Centre*, June 1980, Technical Report TR 142
18 Nriagu, J. O., 'Copper in the environment, Part 1. Ecological cycling', *New York: Wiley* 1979, 128
19 'Toxicological appraisal of halogenated aromatic compounds following groundwater pollution', Report on a WHO Working Group, *Copenhagen: WHO Regional Office for Europe*, 1980
20 Weiss, M., 'The impact of environmental control expenditures on the US copper, lead and zinc mining and smelting industry', Report, National Economic Research Associates, Inc., *New York*, 1978

Treatment before discharge

John M Sidwick and Richard Barnard

Many manufacturing processes use toxic chemicals, often in solution. If not dealt with by the manufacturer these chemicals, or their derivatives, find their way into the trade effluent streams discharging from the industrial premises. The trade effluents pass directly or indirectly to surface water or, less often, to ground water. In order to protect the environment, or treatment facilities such as municipal sewage treatment works, the concentrations and/or loads of any toxic constituents have to be reduced to acceptable levels. The question of acceptable levels for specific chemicals is complex, and other factors must be considered. These include the possible presence of toxic materials from other sources, the nature of the receiving environment and the uses to which it is put, the interaction between one toxic constituent and others that may be present, and the current state of knowledge about toxicity.

Trade effluent survey

If it is required that the toxicity of the effluent be lessened, and if the requirement is reasonable, the toxic constituents must be reduced in concentration, removed altogether, or converted to a less toxic or non-toxic form. Whichever approach is most appropriate and economical will cost money and final decisions should not be taken lightly; they must be based on a thorough understanding of the characteristics of the waste in question, and how it arises. The first step therefore, should be a comprehensive examination of all the waste-related manufacturing processes including flow measurement, sampling and analysis at selected points within the factory as well as at the points of discharge of effluent. As a result of a careful and expert interpretation of the data resulting from a properly designed study, decisions can be made. The main stages of activity available to the designer are shown in Fig 1.

Mr Sidwick is an associate of Watson Hawksley, Terriers House, Amersham Road, High Wycombe, Bucks, and a director of Environmental Resources Ltd. Mr Barnard is a chemist in the Process Design Group of Watson Hawksley

Table 1 **Some common pollutants, their origins and treatment methods**

Pollutant	Type of waste and some sources	Possible treatment methods
Acids	Any mineral or organic acid causing pH depression to < 6 usually requires treatment. Typically: Battery manufacture Steel industry Chemical works	Neutralisation using alkali – typically lime or sodium hydroxide.
Alkalis	Presence of any alkali causing pH to rise to >9 usually requires treatment. Typically: Laundries Textile industry Chemical works	Neutralisation using acid – usually a mineral acid such as sulphuric or hydrochloric.
Ammonia	Usually free ammonia (ammoniacal nitrogen) but combined nitrogen can create problems. Typically: Coke oven effluents Domestic sewage Fertiliser factories	Desorption by air stripping. Nitrification possibly followed by denitrification. Incineration. Chemical oxidation.
Biodegradable waste	Organic wastes with no toxic compounds present. Nutrients may have to be added. Typically: Domestic sewage Food waste	Settlement if necessary. Biological treatment followed by settlement and tertiary treatment if necessary.
Chromium	Chromium often present in hexavalent form which is most toxic. This is soluble as chromate and dichromate. Typically: Plating wastes Chrome tanning Aluminium anodising Boiler water blowdown	Cr^{6+} reduced to Cr^{3+} by electrolysis or chemical reduction prior to removal by coagulation and settlement. Can be removed directly by ion-exchange. Direct precipitation with barium chromate Reverse [illegible]

Table 1 continued

Pollutant	Type of waste and some sources	Possible treatment methods
Cyanide	Exists in solution as CN^- used to hold metal ions in solution. Concentrations vary usually from 20-700 mg/litre. Typically: Ore extracting Plating wastes Coke furnaces	Oxidation using Cl_2 at pH 10 followed by acid hydrolysis then neutralisation. Ion exchange. Electrolytic decomposition.
Metals (in alkaline solution)	May be copper, nickel, cobalt, lead and zinc. Concentrations of metals vary widely depending upon origin. Typically: Metal processing Plating Rayon manufacture (zinc)	Electrolysis. Ion exchange. Reverse osmosis. Neutralisation followed by lime addition.
Metals (in acidic solution)	Most metals exist in acid solution as chloride, nitrate, sulphate. Typically: Metal processing Plating Boiler water blowdown.	Precipitation of hydroxide by lime addition. Ion exchange. Electrolysis.
Oil	Mineral and vegetable oils. May sometimes be present as emulsion. Typically: Engineering factories Oil processing plants Petroleum industry Wool industry	Coalescence – oil layer skimmed off to disposal or incineration, water layer to further treatment if necessary. Air flotation. Centrifugation. Adsorption.
Phenols	Phenols are found in various wastes ranging from 3-10,000mg/litre. Typically: Coke oven effluents Oil refineries Petrochemicals Wood preserving	Methods used depend upon initial phenol concentrations: >500mg/litre – solvent extraction and recovery. 5-500mg/litre – biological treatment. 0-10mg/litre – oxidation using ozone. Activated carbon.
Solvents	Organic solvents such as acetone, benzene, alcohols are often present in waste streams. Typically: Chemical industry Pharmaceutical factories	Desorption by air stripping. Incineration. Carbon adsorption for lower concentrations. Extraction and recovery
Suspended solids	Very variable in nature but present to some degree in most wastes.	Settlement with chemical coagulation, if necessary. Air flotation.

Waste reduction/modification

It is probable that the survey will have identified areas where waste flows or loads can be reduced either by introducing modifications to manufacturing processes or by better attention to operational procedures – 'good housekeeping'. If this is so, and if the changes are of major significance, it might be necessary to repeat all or part of the survey after their implementation.

Laboratory and pilot plant studies

Once the nature of the effluents is known it is likely that possible treatment techniques will need to be studied experimentally. This can often be done by relatively simple laboratory testing: for example, precipitation, flocculation and pH control. Bench-scale work may also be necessary, for example to study the biodegradability of an effluent before and after chemical treatment.

Although laboratory work can enable the designer to select a treatment system, often it is not possible to use this as a basis for final treatment plant design. When this is the case, pilot plant work must be undertaken to test the validity of the conclusions drawn from the laboratory studies.

Treatment plant

Following the various investigations it will be possible to undertake the detailed design of the fullscale treatment plant. If the investigatory work has been carried out competently then the design should ensure a treatment plant that will consistently meet effluent standards cost-effectively.

Methods of treatment

Types of wastewater and the appropriate treatment required can be divided into three broad categories:

- Wastewaters containing only inorganic or toxic organic constituents requiring only one or more physicochemical treatment stages.
- Wastewaters containing biodegradable organic pollutants in addition to inorganic or toxic organic constituents, requiring the removal of the inorganic or toxic organic constituents prior to biological treatment.
- Wastewaters containing only biodegradable substances, requiring solely biological treatment.

This categorisation is very general and there are many permutations within the wide field of effluent treatment. Table 1 lists some of the common pollutants and their origins together with various typical treatment methods. Selection of the appropriate method is based upon many interrelated factors such as capital and running costs, wastewater volume and strength, other components of the waste stream and land availability.

Figure 2 demonstrates how different treatment processes may be incorporated into a single plant designed to treat six different wastewaters. For completeness however, examples of case studies are given from the authors' experience showing the treatment of four very different industrial effluents to different standards by different methods.

Lead-acid battery manufacture

Nature of effluent and effluent standards

Effluent arising from the manufacture of lead-acid batteries has a low pH, due to sulphuric acid, usually in the range 1.5-3.0. It also contains a high level of lead, present in a soluble form, as lead sulphate, and as an insoluble form as lead oxide. The total lead content varies, depending on which manufacturing processes are operating, but typically is within the range 5-50mg/litre.

Treatment of the effluent before it is discharged to the sewer is required for two reasons. Firstly, the acidic nature of the effluent would give rise to corrosion of the sewerage system. Secondly, the lead content would significantly increase the lead concentration in the sludge produced at the sewage works to a point where disposal to land would no

Table 2 **Budget costs for chromium treatment**

	Costs (£) (1977 prices)	
	Capital	Annual running
Electrochemical reduction	103,000	10,000
Chemical reduction	85,000	14,000
Ion exchange	142,000	11,000

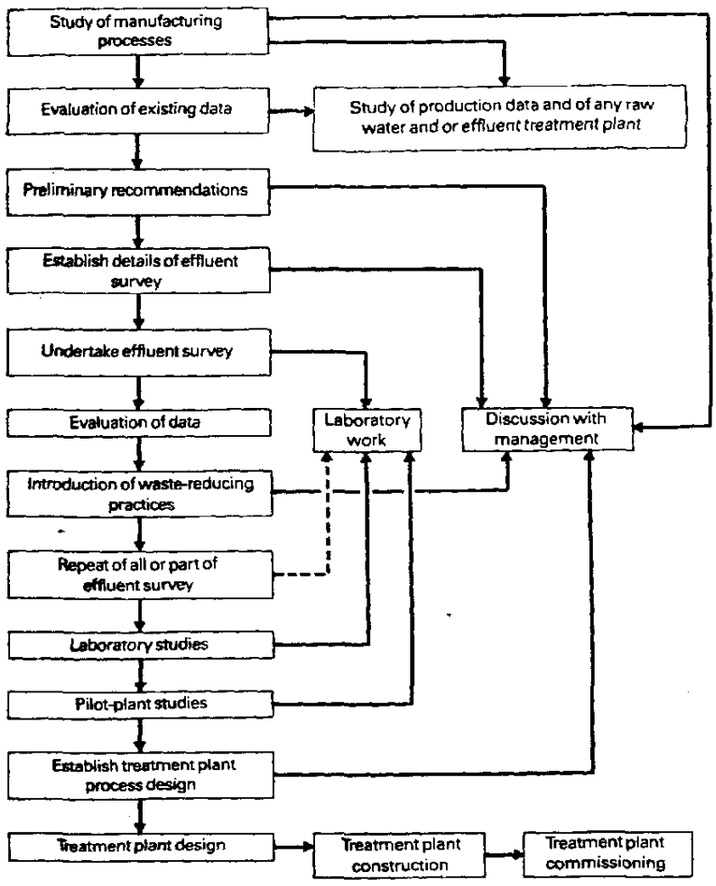


Fig 1 Trade effluent survey - principal activities

longer be possible. A consent standard had therefore been imposed limiting the pH to the range 6-10 and the total lead content to less than 5mg/litre.

Treatment plant

To achieve the required effluent standard a treatment plant was installed which consisted of pH control by lime-slurry addition and solids removal by coagulation and precipitation, followed by sand filtration. An outline of the process is given in Fig 3. Polyelectrolyte was selected as the coagulant aid, the choice of specific polyelectrolyte being determined by site tests. During normal operation the lead is precipitated out as the insoluble hydroxide and removed along with the other solids. If lime precipitation of lead is inadequate, there is provision for adding sodium phosphate to precipitate out the soluble lead as the phosphate. The resultant flocculated solids, including the precipitated lead, are removed in an upward flow sludge blanket clarifier. With this type of plant the blanket density is very high; settling tube tests indicated that an upward flow velocity of up to 5m/h could be sustained and this has been borne out in practice.

The sludge blanket is continuously withdrawn and partly recycled to the flocculation zone. Some, with a solids content of 20,000-50-000mg/litre, is bled off to a sludge thickener where it settles to form an extremely dense sludge. This is then centrifuged and the resulting cake is sold to smelters for recovery of the lead.

Chromium removal from cooling tower blowdown

Cooling tower blowdown containing approximately 5mg/litre of hexavalent chromium had to be treated to 0.1mg/litre for direct discharge to a river in Belgium. Three treatment options (outlined in Fig 4) were considered:

- chemical reduction and precipitation;
- electrochemical reduction and precipitation;
- solids removal followed by ion exchange.

Initially, these methods were assessed on theoretical cost grounds. From the summary in Table 2 it can be seen that chemical reduction followed by precipitation has the lowest capital cost although it is slightly more expensive in terms of

Table 3

Flow (m^3/d)	22,500 ± 3500
Suspended solids (mg/litre) (average)	1000
Suspended solids (90 per cent)	< 1500
Chemical oxygen demand (mg/litre) (average)	2200
Total toxic metals (Cr, Pb, Zn, Cr, Ni) (mg/litre)	10-50
pH	1-11

Table 4

Suspended solids (mg/litre)	150
Total metals (mg/litre)	1
Copper (mg/litre)	0.2
Lead (mg/litre)	0.3
Zinc (mg/litre)	0.5
Chromium (mg/litre)	0.5
Nickel (mg/litre)	0.1
pH	7-9

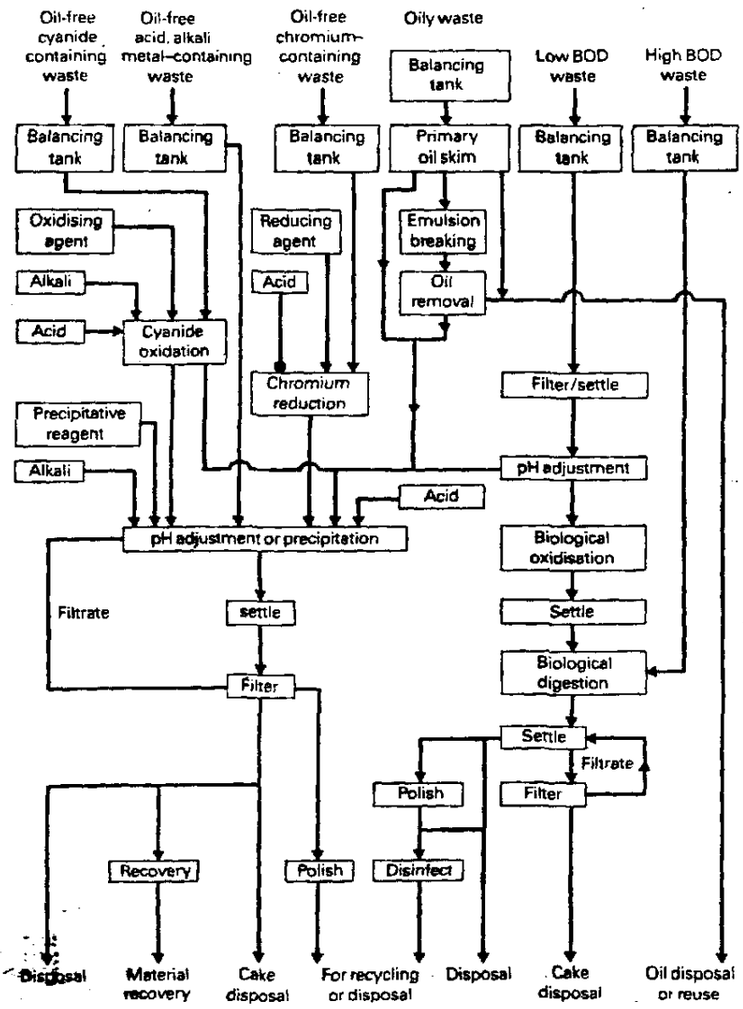


Fig 2 Planning an overall effluent treatment system[3]

running costs. Chemical precipitation (Fig 5) was selected as the most suitable treatment method for this installation.

Chromium reduction is achieved by reacting the acidified effluent with sulphur dioxide. The pH of the effluent is lowered to pH 2.0-3.0 using sulphuric acid, and sulphur dioxide is then introduced to effect chromium reduction by the reaction:

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

After reduction to the trivalent form, the chromium is precipitated out as chromium hydroxide by the addition of sodium hydroxide. The precipitant is separated using a tilted-plate separator, consolidated and dewatered on drying beds.

With a maximum flow of 80m³/h, 24kg/h of 98 per cent sulphuric acid are needed for pH control prior to chemical reduction. Chemical reduction theoretically requires 0.3kg/h of sulphur dioxide under stoichiometric conditions, but assuming a worst condition in practice of 30 per cent utilisation, the facility is available for the addition of 1.0kg SO_2/h. pH control after reduction requires 40kg/h of 50 per cent sodium hydroxide.

In terms of effluent quality, chromium concentration is reduced from the original 5mg/litre level consistently to less than 0.1mg/litre. This degree of removal generates 50-60mg/litre suspended solids (SS) after precipitation, which at 95 per cent suspended solids removal efficiency results in the separation of 4.56kg dry solids/h. The separated sludge readily consolidates to about 2.5 per cent dry solids giving a daily sludge production of 4.5m³. Dewatering to about 20 per cent dry solids is readily achieved on the drying beds resulting in 0.55m³/d of dewatered sludge for disposal. The dewatered sludge is periodically removed to tip. Some specific points are worthy of note:

- To reduce handling and to take advantage of bulk purchase, sulphuric acid is stored in a 15t storage vessel.

Table 5 Interface settling rates

Experiment No.	pH	Suspended solids (mg/litre)	Interface settling rate (m/h)
2	10	1520	1.73
3	8	1590	1.56
4	8	1120	2.08
5	10	1840	1.16
6	10	2130	0.92
7	8	2130	1.10
8	10	1570	1.83
9	8	1320	
10	10	1130	1.60
11	8	1160	1.32

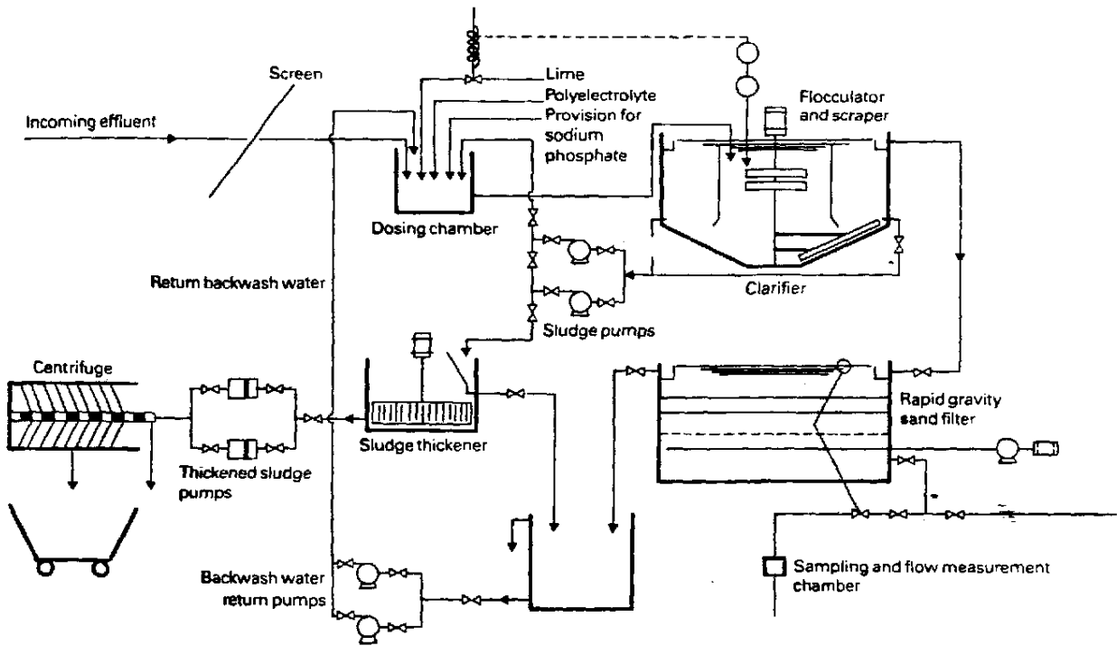


Fig 3 Pre-treatment for effluent from battery manufacture

● Sodium hydroxide was selected for pH control because of local availability and relatively low capital costs; often lime would be more appropriate.

● The use of sodium hydroxide eliminated the need for storage silos, slurry tanks and dosing problems; the sodium hydroxide is simply dosed using small metering pumps.

● Tilted-plate separators were selected for the removal of the precipitate, largely because of shortage of land area; often simple gravity separation would be adequate.

● The facility was incorporated for the addition of polyelectrolytes to aid solids separation.

Manufacture of dyestuffs

As a result of changing local circumstances and proposals to make effluent standards more restrictive, it was necessary to consider pretreatment of an effluent from the manufacture of dyestuffs. The effluent was discharged to the public sewer and contained high concentrations of toxic metals. The imposition of more stringent standards was due to the abandonment of the chemical precipitation practised at the sewage treatment works, and a change in sludge disposal practices by the sewage works.

The flow and characteristics of the factory effluent are

Table 6 **Effects of settling on toxic metal concentrations**

Total metals	Expt no.	pH adjustment	Metal levels before settling (mg/litre) Cu	Pb	Zn	Cr	Ni	Fe	Mn	Al	Metal levels after settling (mg/litre) Cu	Pb	Zn	Cr	Ni	Total	Fe	Mn	Al
17.5	2	11.5-10.0	2.0	1.5	4.0	2.0	8.0	190.0	13.0	20.0	< 0.5	< 0.5	< 0.5	< 0.5	1.0	< 3.0	1.0	< 0.5	1.0
17.0	3	11.5-8.0	2.0	1.5	4.5	2.0	7.0	200.0	12.0	16.0	0.19	< 0.5	0.13	< 0.1	1.5	< 1.97	1.2	1.5	2.0
9.09	4	9.1-8.1	0.92	0.57	3.0	2.0	2.6	256	3.2	46.0	0.08	< 0.1	0.13	< 0.1	0.7	< 1.11	1.0	0.24	1.0
12.09	5	9.1-9.9	1.24	0.95	3.9	3.0	3.0	450	5.6	58.0	0.06	< 0.1	0.20	0.1	0.7	< 1.17	4.7	0.12	13.0
31.1	6	10.4-10.0	18.8	1.1	4.4	2.8	4.0	90.0	2.5	8.0	1.3	ND	0.2	ND	0.6	2.1	1.2	0.1	ND
38.7	7	10.4-8.0	23.0	1.3	5.9	3.8	4.7	127.0	3.8	10.0	3.1	ND	0.1	ND	0.6	3.8	0.4	0.8	1.0
49.8	8	11.2-10.0	27.0	0.6	18.6	1.8	1.8	8.0	66.0	3.0	3.0	0.1	0.6	1.0	0.5	5.2	2.0	1.0	ND
46.8	9	11.2-8.0	15.0	0.5	27.0	2.0	2.3	56.0	47.0	7.0									
22.6	10	11.1-10.0	6.2	0.6	10.6	1.1	4.1	100	18.5	12.0	0.9	ND	0.2	ND	0.7	1.8	1.8	0.4	1.0
23.0	11	11.1-8.0	5.9	0.7	11.1	1.2	4.1	106	19.5	12.0	1.2	0.1	0.2	0.1	0.6	2.2	0.8	5.4	ND

Table 7 **Canvas cloth case study – analytical data**

Source	BOD(*)	COD	SS	TDS @ 110°C	TDS @ 600°C	Amm. N	Total N	Total P	Oil & grease	Syndet	pH	Cl^-	SO_4^{2-}	S^-
Mixed sulphur and vat dye effluent	715	2500	260	5500	4500	0.1	30	2	23	10	4.6–7.0	470	1850	350
Bleaching and direct dye effluent	535	3720	120	20,500	15,000	11	109	3	19	3	12.5	1250	1250	5
Sulphur dye effluent	1180	4024	490	8500	5800	2	55	10	20	15	5.2	370	1950	365
Water and rotproofing effluent	1200	36,000	46,000	49,000	1800	35	310	—	270	0.1	4.3	220	25	Tr

(*) BOD test carried out without seeding
All data reported in mg litre except pH

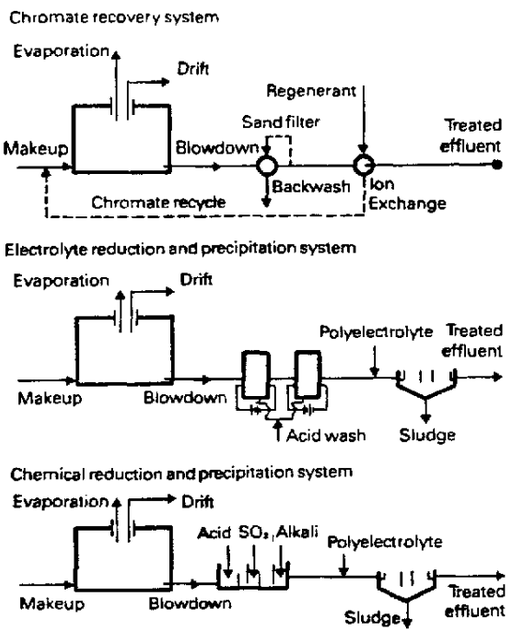


Fig 4 Alternative methods for treating cooling tower blowdown

summarised in Table 3. Quality of the effluent varies widely, particularly with regard to pH. The standards being sought by the receiving Authority are summarised in Table 4. The standards set reflect the Authority's concern about toxicity, particularly of sewage works primary sludge, rather than about organic pollution load.

Experimental studies

In order to meet the standards it was proposed that the effluent should be treated by controlling pH and then by sedimentation, with sludge dewatering and disposal of sludge to tip. To confirm this judgment and refine process design, experimental work was undertaken to examine:

Table 8 **Discharge limits to sewer**

Parameter	Maximum permitted concentration (mg/litre except pH)
BOD	400
COD	600
SS	400
pH	6-9
S^- (as S)	1
SO_4 (as S)	600
T.d.s.	3000

- the optimum pH for sedimentation and metals removal;
- settling rates and retention time for sedimentation;
- the effect of polymer addition;
- methods of sludge dewatering.

Suspended solids removal. Long-tube settlement tests were undertaken in the laboratory after adjustment of pH to either pH 8.0 or pH 10.0; the optimum pH range based on theory and experience. The results of a number of tests given in Fig 6 show that settlement of the effluent, after pH adjustment, is capable of reducing the suspended solids concentration to well within the proposed limit of 150mg/litre. The suspended solids concentration after 90min settlement ranged from 20 to 60mg/litre with an average of 38mg/litre. This degree of settlement also reduced oxygen demand, showing an average chemical oxygen demand (COD) reduction of 15 per cent.

During the long-tube settlement tests, measurements were also taken of interface settling rates; some results are shown in Table 5. With one exception, the interface settling rate equalled or exceeded 1.1m/h.

Metals removal. Table 6 shows the effect on toxic metal concentrations of settling the effluent for 90min; 10 experimental runs are shown. In Fig 7 curves are presented for two of the runs, together with brief data on the effect of extended settlement. The experimental results show that total metal levels after 90min settlement were within the range 2-7mg/litre with an average of 2.8 and 3.5mg/litre at pH 10 and pH 8 respectively. This suggests that a pH level much above pH 8

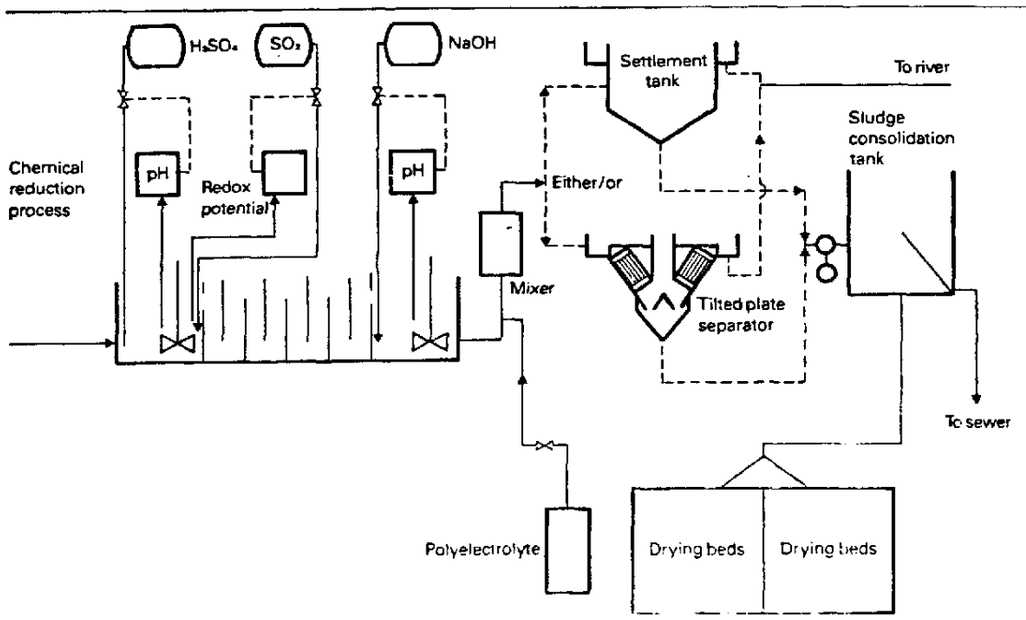


Fig 5 Outline of chemical reduction and precipitation process

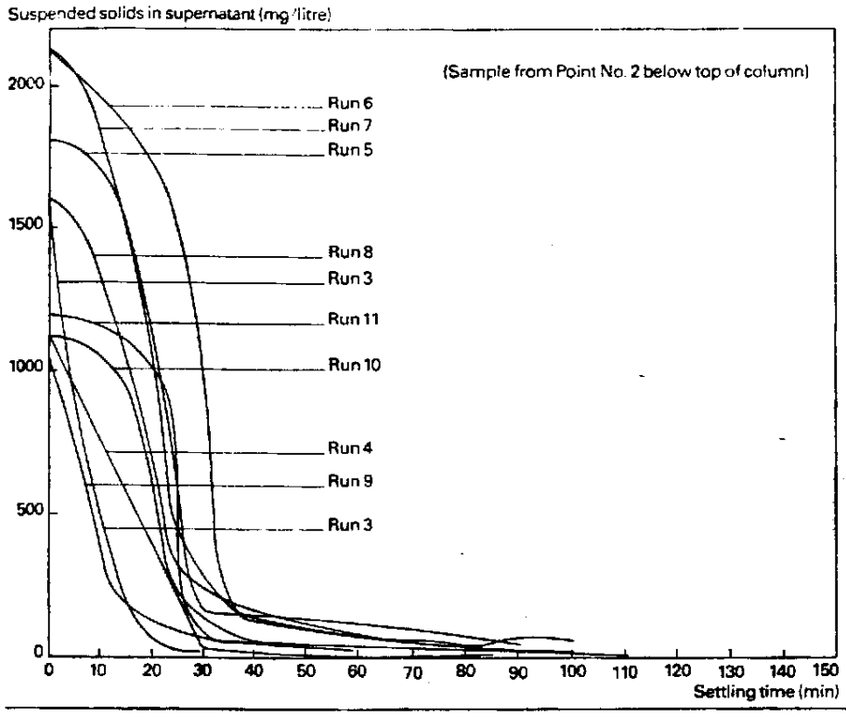


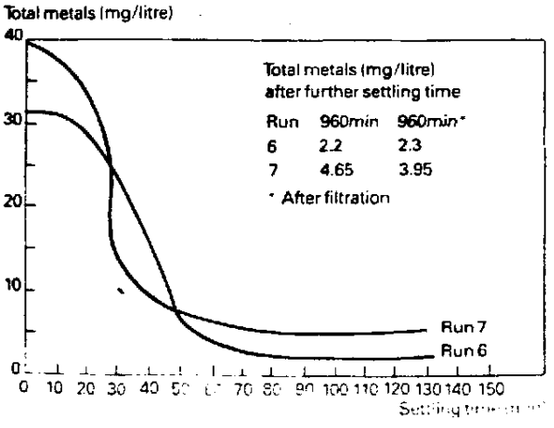
Fig 6 Effect of settling time on suspended solids removal

is not critical for metals removal and that extended settlement time and filtration would not reduce metals concentration significantly.

A study of the data showed that the proposed limits for lead, zinc and chromium were generally being obtained but that those for copper and nickel were being exceeded due, it was thought, to the presence of soluble metal complexes. The work suggested that the proposed limits could not be obtained by conventional precipitation and settlement.

Effect of polymers. The effects of anionic, cationic and non-ionic polymers were studied using long-tube settling tests. It was found that, while the effects were often good, the same polyelectrolyte was not effective on all samples. Dosage rates were variable and running costs could be high. It was concluded that reliance could not be placed on polymer addition but that polymers could be regarded as a possible means of upgrading the plant performance or capacity if shown to be effective on full-scale.

Fig 7 Effect of settling time on metals removal



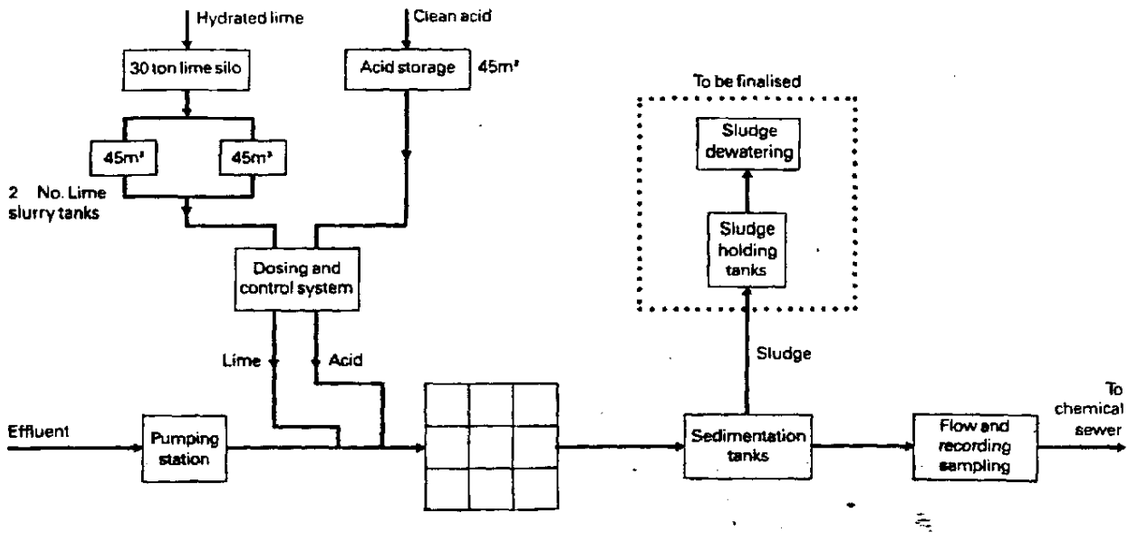
Sludge dewatering. There were overriding reasons related to sludge disposal that demanded a dry, firm sludge cake. Preliminary experimental work showed that this could not be achieved using centrifuges or vacuum filters. Detailed experimental work was therefore restricted to pressure filtration, possibly preceded by thickening by vacuum filtration or centrifugation. Preliminary tests were undertaken in the laboratory using a small compression cell. Subsequently, full-scale trials were undertaken at a local sewage works. This work showed that filter pressing on conventional plate presses was suitable for dewatering the sludge providing they were operated at a minimum of 5.5bar. At this pressure, it was expected that a feed sludge of 5 per cent dry solids would result in a sludge cake of 40-45 per cent dry solids. Similar results were obtained with a 7.5 per cent dry solids feed but pressing time was shown to be reduced by nearly 40 per cent. For this reason gravity thickening of the sludge was thought to be necessary.

Full-scale treatment plant

As a result of the experimental studies, a full-scale treatment plant was constructed. Figure 8 depicts the plant schematically and also shows the basic process design parameters. The following comments may be useful.

pH control. pH is controlled by the addition of lime or sulphuric acid to achieve a pH of about 8.5. pH 8.5 was judged to be the optimum in terms of cost-effectiveness since any increase above this level would offer very rapidly diminishing returns in terms of metals removal. Post-neutralisation facilities were not included because it was expected that the pH standard would be attained without them.

Sedimentation tanks. Sedimentation tank design was related to both suspended solids removal and toxic metal removal. It was judged that there would be little difficulty in [illegible]



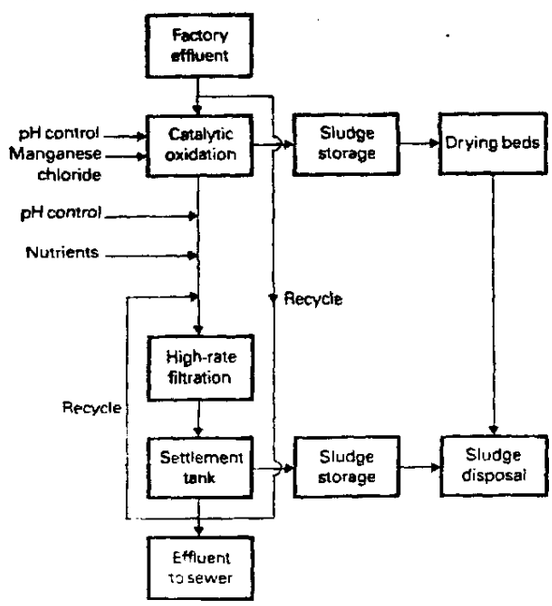
URL 03706

Fig 8 Process summary

	Pump capacity	pH control tanks (3 stage)	Sedimentation tanks Area	U/F velocity
Immediate design:	2 No. Variable speed each 238 litre/s (4.5mg/d) 1 No. Fixed speed 238 litre/s (4.5mg/d)	2 No. Duty streams each 214m³ 1 No. Standby stream 214m³ Duty capacity 15min. retention at max. pumped flow 475 litre/s (9mg/d)	1545m²	1.1m/h 1.67h
Long term design:	2 No. Variable speed each 315 litre/s (6mg/d) 1 No. Fixed speed 247 litre/s (4.7mg/d)	3 No. Duty streams each 214m³ 1 No. Standby stream 214m³ Duty capacity 17 min. retention at max. pumped flow 630 litre/s (12mg/d)	2066m²	1.1m/h 1.67h

the suspended solids standard of 150mg/litre but that more conservatism was needed to offer maximum practicable reduction of toxic metals concentrations as, even under laboratory conditions, the required standard could not be met. Thus, peak design flow was related to a surface loading less than the solids/interface settlement rate established experimentally. An 85 per cent order of probability could be expected to offer a reasonable basis for plant design. Bearing in mind that the full-scale plant might be expected to give a better efficiency than the experimental work, a figure of 1.1m/h surface loading was eventualy selected. Additionally, a retention period of 1.7h was selected at maximum design flow since this corresponded to the minimum period required for effective metals and suspended solids removal; longer retention periods showed no significant improvement (Fig 7).

Fig 9 Flow diagram of canvas cloth effluent treatment plant



Operational experience with full-scale plant. The full-scale treatment plant was commissioned in 1979. Since that date, it has essentially operated well although there have been some inevitable teething problems.

Textile mill effluent

Apart from the possible presence of particularly toxic dyes, textile effluents are normally non-toxic and readily treatable using normal biological treatment techniques. However, in this case, the effluent contained a high concentration of sulphide.

Nature of effluent and effluent standards

The effluent arises from the manufacture of canvas cloth for military purposes and its subsequent processing. The cloth is manufactured from grey yarn and, after weaving, it is bleached, dyed and proofed; 45m³/d of effluent are generated. Average analytical data for the principal effluents are given in Table 7. The proposed standards for discharge are complex, but the principal limits are presented in Table 8.

Effluent treatment

Sulphide removal. The main problem was thought to be sulphide removal and a number of possible methods of treatment were considered. Sulphide can be removed by acidification and aeration but this method was discounted because it merely changes a water pollution problem into one of air pollution, unless very costly treatment of the gaseous hydrogen sulphide is practised.

Sulphide can be precipitated chemically using ferrous sulphate and lime but the resultant sludge is difficult to settle and dewater, and chemical costs are high. For these reasons chemical precipitation was not considered further.

Chlorination is also possible, oxidising sulphide to sulphate. However, large quantities of chlorine are needed to avoid the production of unsettleable colloidal sulphur and in consequence operating costs are high. Again this option was discounted.

The remaining option was catalytic oxidation. This technique was judged to be the most appropriate on both technical and cost grounds. The system proposed consisted of batch treatment by aerating the waste with 50-100mg/litre of manganese (as manganese chloride) at pH 10 to reduce sulphide to a negligible level. A manganese hydroxide precipitate requiring settlement and disposal was produced. The settlement of manganese hydroxide ensured that suspended solids concentrations were acceptable. pH had to be controlled after oxidation and achieving the pH limit presented no problems.

Sulphate and total dissolved solids. The treatment of the effluent to reduce sulphate and total dissolved solids concentrations was thought to be impracticable. It was proposed that sulphate should be reduced by introducing modifications to factory processes and that negotiations should be commenced to persuade the receiving Authority to relax the total dissolved solids standard.

The only remaining difficulty was the biological oxygen demand (BOD) limit but, after catalytic oxidation the effluent was biodegradable and therefore high-rate biological treatment was recommended to reduce the BOD to the required level. A schematic diagram of the treatment plant is given in Fig 9.

Reference

1 Bridgwater, A. V., & Mumford, C. J., 'Waste recycling and pollution control handbook', *London: George Godwin* 1979

See following article

Disposal to sea of toxic materials

John E Portmann and Michael G Norton

For many years, both industry and control authorities have thought that because of its size, the sea could accommodate vast quantities of waste material without any ill-effects. Experience in the wake of Minimata, the brown pelicans off California and the Eider ducks near Rotterdam has shown that this is not so. It is now recognised that although the sea does have a capacity to accept certain toxic materials without suffering any ill effects to its flora and fauna, it can only do so if due attention is paid to the method of disposal used, the rate of dilution and dispersion, and the possible mechanisms for aggregation of the waste or its reconcentration by biological systems. In the light of this, a number of control measures on what can be discharged to the sea have been introduced at both international and national level.

International controls

Dumping

In 1972 two Conventions were agreed to control pollution of the sea by dumping of wastes from vessels. The first was the Oslo Convention[1] which was signed by 13 states and applies to the North Sea and north-east Atlantic Ocean. Later, the London Convention[2] which applies to all the World's seas and oceans was signed by 60 states. Both Conventions are in force following their ratification by the required number of states.

The form of the two Conventions is similar, each listing substances for which dumping is prohibited and substances for which dumping is strictly controlled; the dumping of remaining substances must be controlled under licences, having regard to a number of factors including the composition and properties of the waste, the characteristics of the proposed dumping area and the method of disposal. These latter factors are listed in Annex III of the Conventions and must be considered in every permit application. Broadly speaking, they are a form of 'check list' to ensure that the national licensing authority considers all the relevant information necessary to estimate the environmental impact of the proposed disposal operation. Additionally, in considering the sea for the disposal of waste, states also undertook to take into account the practical availability of alternatives to sea disposal. The degree of consideration afforded to any of these factors varies according to the nature of the waste and the scale of the proposed dumping operation and it is not usually necessary to take all factors into account.

The Conventions list certain materials which require special care (Annex II) and others for which dumping is prohibited (Annex I). These latter materials, the so-called 'black list' substances, include: mercury and its compounds, cadmium and its compounds, organohalogen compounds, carcinogens, persistent floatable plastics and (in the Oslo Convention only) organo-silicon compounds other than polydimethylsiloxanes. The member states are required to prohibit the dumping of any waste containing these substances except where they are present in only 'trace' quantities or additionally, in the case of organohalogen or organosilicon compounds, when they are 'non-toxic' or are 'rapidly converted in the sea into substances which are 'biologically harmless''. Relaxation of the Annex I prohibitions is thus possible, provided that the discharge of the waste is not harmful to the marine environment. Where a licensing authority considers that a waste

Dr Portmann and Dr Norton are at the Ministry of Agriculture, Fisheries and Food, Directorate of Fisheries Research, Fisheries Laboratory, Burnham-on-Crouch, Essex