

WASTE WATER IN THE NON-FERROUS METALS INDUSTRIES THE SCOPE FOR RECYCLING

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Abstract—Substantial quantities of water are used in the non-ferrous metals industries for rinsing work after it has been pickled to remove oxide scales and for scrubbing gases to remove contaminating dusts and fumes. Such contaminated waters are usually treated with lime or other alkali to neutralise acid and precipitate metal hydroxides before they are discharged. This procedure has changed little over the past decade, although the separation of the hydroxide floc by flotation rather than settling has made some progress.

Some authorities are now proposing effluent standards which will be difficult to meet by the conventional practice. Furthermore there are increasing difficulties in disposing of the metal hydroxide sludge which arises. Although this contains valuable metals, recovery is difficult.

An analysis of the situation suggests that with the present high cost of water and taking into account the charges frequently levied for accepting treated effluent water, emphasis should be placed on recycling rather than merely treating effluents to a standard acceptable for discharge. Despite the high capital cost of the plant, ion-exchange now looks economic for treating pickle rinse waters, since the water can then be recirculated. Reverse osmosis is another possibility and one large plant is said to be under construction. Taking account of the value of the recycled water, such processes now appear more economic than conventional lime precipitation.

With suitable changes in pickling practice to allow the pickles to be regenerated there is the distinct possibility of a complete closed-loop in which rinse water is recycled and metals are recovered electrolytically.

In order to assess the magnitude of the use of water in the non-ferrous metals industry and to determine the scope for economies, a survey was made of the water usage in five wrought aluminium plants and eleven copper and copper alloy manufacturing plants in the United Kingdom. With the assistance of the International Wrought Copper Council, this survey was extended to thirty-three copper manufacturing plants in ten other European countries. A summary¹ of the water usage in each of the plants manufacturing copper and copper alloy products is given in Table 1. It was deduced from this survey that about 95 m³ of water is required to produce 1 tonne of copper or copper alloy semi-manufactured product i.e. plate, sheet, strip, rod, wire tube etc. This is somewhat more than the amount of water used in the steel industry (50 m³/tonne), rather less than is used in the paper industry (155 m³/tonne) or the synthetic fibres industry (133 m³/tonne) and comparable to the wallboard industry (98 m³/tonne).²

Analysis of the returns reveals that a large proportion of the water is used for cooling purposes. In fact, in the aluminium semi-fabricating industry this accounts for over 95% of the total requirement. The returns from the U.K. copper industry showed that about 75% of the water is used for cooling, and although the proportion positively identified as for cooling was less in other countries, the use of a substantial proportion of the water was not identified and, might well be for cooling. This cooling water is used for extracting heat from moulds in which metal is cast, for cooling furnaces, for cooling rolls, compressors and other ancillary equipment.

For the most part, this water is contaminated only with heat and it is therefore possible to recirculate the water for re-use after the heat has been removed. It is in this direction that there is the greatest scope for water economy. Cooling water, treated if necessary to prevent scale formation and corrosion, may be recirculated almost indefinitely if a suitable heat exchanger is included in the

circuit. At the time at which this survey was made, about five years ago, the proportion of water recirculated showed great variation from firm to firm, approaching 100% in a few cases down to virtually nil in many instances. It is believed that increasing water costs together with the difficulty of abstracting more water from wells, lakes, rivers and canals to meet the demands of increasing production, have considerably changed the situation and that a much greater proportion of cooling water is now recirculated, thus reducing the demand on water resources.

CONTAMINATED WASTE WATER

In the copper semi-fabricating industry, there is a substantial demand for water for rinsing work after it has been acid pickled. This demand is almost totally absent in the aluminium industry where the oxide film formed when the metal is heated for manipulation in various ways is protective and remains thin and scarcely visible. Water used for pickle-rinsing is contaminated with the pickle liquor itself, in the case of copper and its alloys mainly sulphuric acid sometimes assisted by an oxidising agent such as sodium bichromate, and with metal salts. It may be seen that rinse water accounts on average for about 20% of the water consumption in the copper semi-fabricating industry. In individual firms it can rise to over 90% of the water demand depending on the nature of the product. Reliable figures are difficult to obtain, but the water consumed for pickle-rinsing in the U.K. copper and copper alloy industry is probably of the order of 10 M m³/annum. The demand for water for rinsing purposes in the metal finishing industry of the U.K. has been estimated as between 50 M m³ and 150 M m³ per annum. Because of its acidity and more particularly because of contamination with heavy metals such as copper, zinc, nickel, lead etc. this rinse water is unacceptable for discharge to public sewers or inland waters without costly preliminary treatment.

Table 1. Summary of water usage in countries surveyed (copper industry)

Country	UNITED KINGDOM		GERMANY		ITALY		OTHER COUNTRIES	
	Million cubic metres per annum	%	Million cubic metres per annum	%	Million cubic metres per annum	%	Million cubic metres per annum	%
Annual consumption	13.52	100	7.45	100	26.92	100	18.69	100
Mould cooling	5.35	39	1.62	21.8	1.58	5.8	1.69	9.1
Roll cooling	0.33	2.5	1.52	20.6	2.47	9.2	3.90	20.9
Furnace cooling	3.18	23.5	0.99	13.3	6.20	23.3	2.72	14.4
Compressor cooling	1.14	8.5	0.23	3.1	0.51	1.8	0.70	3.6
Quenching	0.44	3.5	nil	0.0	0.15	0.5	0.28	1.5
Pickle-Rinse	1.39	10.5	1.12	15.0	5.10	19.0	3.77	20.2
Steam raising	0.07	0.5	0.08	1.1	0.10	0.4	0.97	5.2
Hydraulic power	1.29	9.5	0.10	1.3	5.60	20.8	neg.	0.1
Domestic	0.14	1.0	0.59	7.9	0.36	1.2	0.55	3.0
Miscellaneous	0.19	1.5	1.20	15.9	4.85	18.0	4.11	22.0
Recirculated	3.77	27.9	3.30	43.0*	2.96	11.0	1.82	9.7

* From a single plant.

There is another and possibly growing source of contaminated waste water brought about by the requirement to avoid atmospheric pollution. Both primary smelters and those dealing with secondary metals inevitably generate gaseous products which are contaminated with metal oxide fume and sometimes with chlorides and fluorides. Waste gases similarly contaminated also arise in remelting operations. In most countries, it is now inadmissible to discharge such products to atmosphere without purification to reduce metal fume, chlorides, fluorides etc. to a level at which they are considered to be innocuous and, frequently, invisible. This fume etc. is mainly sub-micron in particle size and it can only be effectively collected with filtration plant of the highest efficiency. Suitable plant includes high efficiency wet scrubbers of the venturi type and, though less common, irrigated electrostatic precipitators. Although the water used for scrubbing is recirculated, there is obviously a need to bleed off contaminated water and to remove from time to time, the sludge of metallic oxides etc. which accumulate. Thus we have an example of an environmental problem in one sphere giving rise to a pollution and waste disposal problem elsewhere.

TREATMENT OF WASTE WATER

At the time the original survey was made, most plants outside the U.K. which made returns seemed able to

dispose of their effluent for little or no expenditure, presumably by making use of local rivers, lakes or canals. It is apparent that this state of affairs has changed dramatically over the past few years with pressure from the environmental lobby and the need to preserve supplies of potable water.

The simplest method for dealing with contaminated effluent is by dilution and this has possibly militated against the recirculation of cooling waters. They were a convenient way of diluting effluent to an extent such that the contamination was less obvious. Such measures can rarely lower the degree of contamination to an acceptable level. More heroic steps are needed.

The conventional treatment is neutralization of the acid and precipitation of the heavy metals as hydroxides. Lime, added as a slurry, is usually found to be the cheapest reagent, but sodium hydroxide or even sodium carbonate have also been used. The latter is possibly less desirable because the carbon dioxide generated tends to hinder the settling of the hydroxide precipitate. Where sodium bichromate is used as an oxidising agent in the pickle, the chromium has first to be reduced to the trivalent state, usually with sulphur dioxide. Many plants, of greater or less complexity, have been installed for treating effluents from copper and copper alloy manufacture, flow sheets for a relatively simple plant and a more complex plant being given in Figs. 1 and 2.³ One drawback

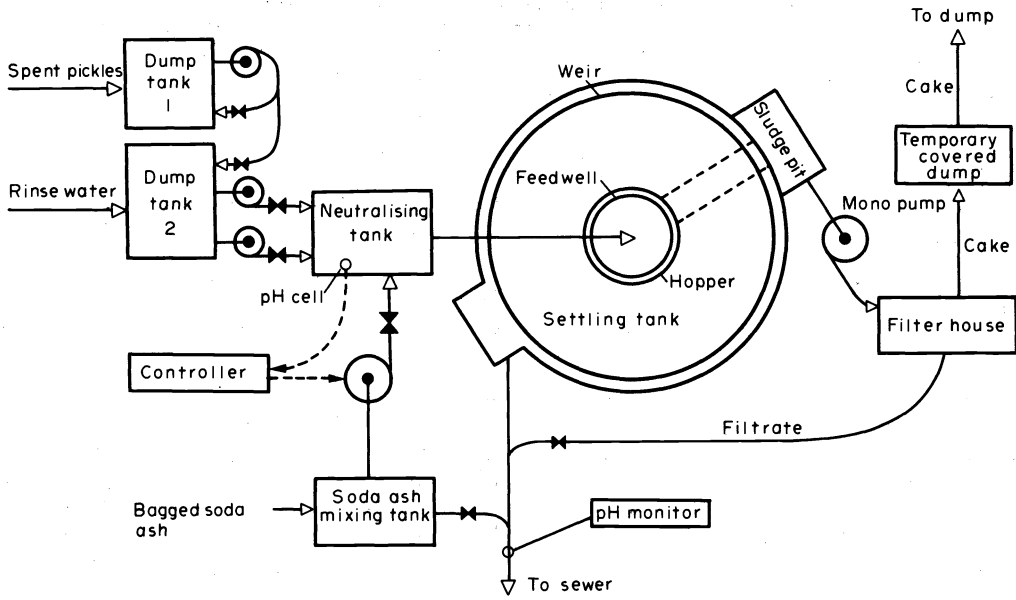


Fig. 1.

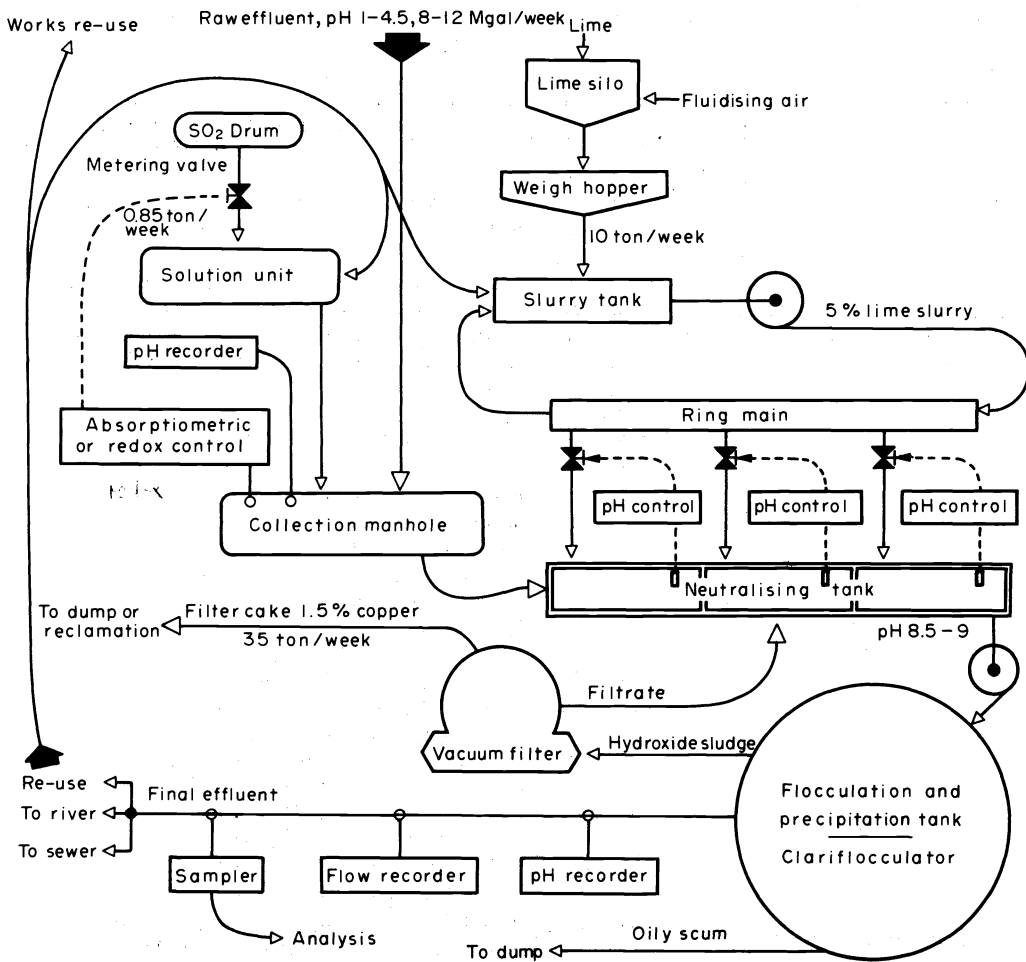


Fig. 2.

Table 2. Water consumption in cubic metres $\times 10^3$ per annum for aluminium industry (U.K.)

Annual Consumption	Mould Cooling	Oil Cooling	Compressor Cooling	Miscellaneous Cooling	Furnace Cooling	Rinse Water	Soluble Oil Make-up	Domestic
9,200	4,550	2,770	200	-	-	140	15	210
1,180	820	-	300	25	3	15	1	27
2,190	-	(2,500)	73	-	-	-	-- 2,500 --	-
2,000	960	100	41	390	160	27	9	54
740	680	-	-	-	-	-	11	50
Total 15,300	7,000	3,180	480	420	167	190	40	420
% 100	45	21	3	2.5	1	1	-	2.5

to this system is the lengthy retention time needed for settling the precipitated metal hydroxides which results in large, space consuming settling tanks. The alternative flotation processes using air bubbles to carry the suspended solids to the surface are claimed greatly to reduce the space requirements.⁴

Many plants for treating effluents arising from pickling processes were built for the U.K. copper industry and elsewhere in the early 1960's along the above lines, when the prime consideration was to improve the quality of the effluent to a level acceptable to public authority sewage systems or, in some cases, to a level at which discharge to inland waters was permitted. These plants have done much to lower the contamination of water courses, but various factors are combining to make it advisable to reconsider the situation.

Firstly in some countries, for example, the United States and Italy, authorities are proposing effluent discharge standards which are difficult, maybe impossible, to meet by the conventional process. Secondly, the precipitation process gives rise to quantities of hydroxide sludge which is becoming increasingly difficult to dispose of. Thirdly, the high cost and increasing scarcity of water, together with the levy of charges for accepting treated industrial effluent suggest that the economics of the process now compare unfavourably with other more sophisticated treatments which allow the water to be recycled.

EFFECTIVENESS OF PRECIPITATION TREATMENT

Data on the solubility of the heavy metal hydroxides are rather sparse and indicate that the solubility may be highly sensitive to pH and affected by the presence of other soluble salts. The factor of principal interest is the concentrations of heavy metals likely to be present in the overflow from a settling tank; part of the metal is in solution and the remainder in suspension. Experiments carried out on the lime treatment of synthetic pickle-rinse solutions under somewhat idealised conditions are illustrated in Figs. 3-5.³

These indicate that the pH to which neutralization is usually carried, around 8-8.5, the limiting concentration of copper in solution is in the region of 0.2-0.4 ppm; for zinc the figure is 1.0-3.0 ppm; while for nickel it is 0.5-1.0 ppm. In the case of nickel and zinc, the concentration of metal in solution tends to fall as the pH rises to about pH 10 (though the reverse was found to apply with chromium). In practice, it is possible that somewhat higher figures would be obtained depending on the extent to which reaction with the lime was carried to completion. However, these concentrations are already higher than have been suggested as standards in some countries.

In practical effluent treatment, the separation of the precipitated metals is always less than perfect, so that to the metal in solution it is necessary to add metal in suspension. A not uncommon figure in the U.K. for the

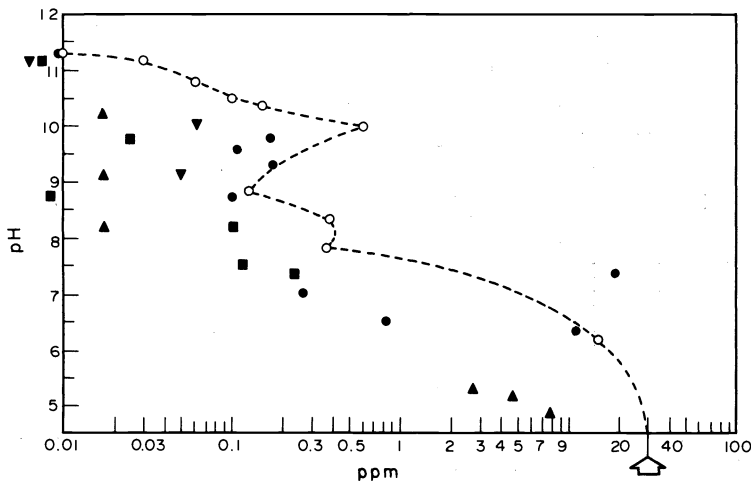


Fig. 3. Residual concentrations of cupric ion in solution after lime treatment. Initial concentration of copper was 30 ppm. Registers off graph denote concentrations below limit of detectability. --○-- Copper alone; ■ With zinc; ▲ With zinc and chromium; ▼ With zinc and nickel; ◆ With nickel.

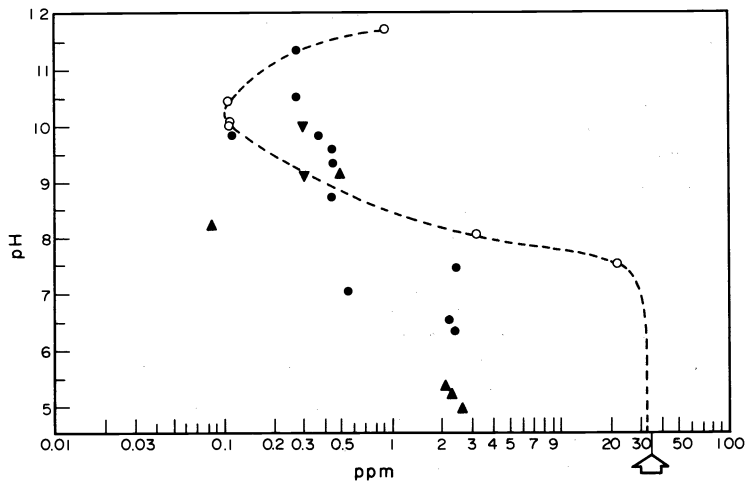


Fig. 4. Residual concentrations of zinc ion in solution after lime treatment. Initial concentration of zinc was 33 ppm. Registers off graph denote concentrations below limit of detectability. --○-- Zinc alone; ● With copper; ▲ With copper and chromium; ▼ With copper and nickel.

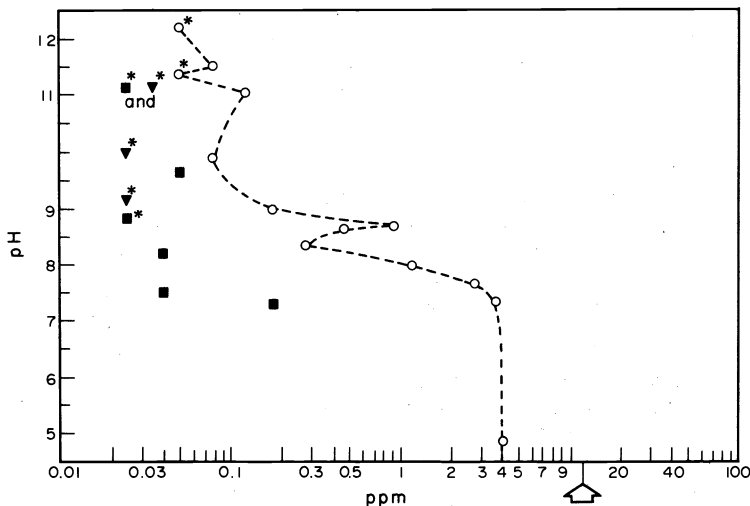


Fig. 5. Residual concentrations of nickel ion in solution after lime treatment. Initial concentration of nickel was 12 ppm. Asterisks indicate minimum detectable concentrations. --○-- Nickel alone; ◆ With copper; ▼ With copper and zinc.

acceptable total of heavy metals in solution and in suspension is 30 ppm. This can be achieved readily. With good settling facilities about half this is reasonably practicable and the amount of metals in suspension could no doubt be reduced considerably by sand filtration. One published account⁵ of the limits alleged to be under consideration by the U.S. Environmental Protection Agency for the metal finishing industry, summarised in Table 3 makes it clear that compliance would require a considerable improvement over the performance to be expected from a conventional lime precipitation treatment plant. The necessity for these stringent requirements, which are in general more restrictive than those for drinking water, is open to debate, but it is doubtful whether the requirements could be met by a lime precipitation plant under industrial conditions.

SLUDGE DISPOSAL

Precipitation treatments give rise to a metal hydroxide sludge with a very high proportion of water. It has been estimated that more than 100,000 tonnes per annum of such sludge is produced in the U.K. from the metal

Table 3. Suggested discharge limits for the USA metals industry²

	Discharge Limits (mg/l)	
	Existing Treatment Plant	New Treatment Plant
Total suspended solids	50.0	10.0
Arsenic	0.1	0.05
Cadmium	0.2	0.1
Chromium (VI)	0.1	0.05
Chromium (III)	0.1	0.05
Total chromium	0.5	0.25
Copper	0.5	0.2
Lead	0.1	0.05
Nickel	2.0	1.0
Silver	0.05	0
Zinc	1.0	0.5
Ammonia	2.0	1.0
pH	6-8.5	6-8.5

finishing industry and from the pickling of copper and copper alloys. To make this easier to transport, the sludge is often passed through a filterpress or rotary vacuum filter, producing a filter cake still containing about 70%

water, but sufficiently solid to handle. Not all of the sludge is filtered; some is taken away in road tankers and dumped. It has been estimated that in the U.K. about 30,000 tonnes per annum of filter cake is produced from the copper and copper alloy industry together with the metal finishing industry. Although this filter cake contains valuable metal it has little or no commercial value and most of it is simply dumped. The high moisture content is probably the main reason why the filter cake is unattractive to the secondary metal refiner, coupled with the fact that the cake usually contains a mixture of metals. Quantitative information is difficult to obtain, but the amount of metal wasted in the U.K. is probably of the order of 1000 tonnes/annum of copper and a comparable quantity of zinc plus considerable amounts of nickel. The conservationist would no doubt deplore this loss of metal but of equal concern to the industrialist is the fact that sites for dumping such residues are becoming increasingly rare. Frequently the residues must be conveyed over long distances, incurring high transport charges, to an approved site where it is considered that leaching of the residues by rain water can cause no harm to water resources.

Much thought has been given to recovering metal from filter cake. Re-solution of the metal hydroxides, followed by separation of the metals and recovery by solvent extraction procedures is one interesting possibility. However, even at the high metal prices that were ruling a few months ago, the economics of the recovery process have not been sufficiently attractive to encourage commercial exploitation. The problem of disposing of large quantities of hydroxide sludge seems to be an inherent drawback to the conventional effluent treatment process and one which is becoming increasingly urgent.

ECONOMICS OF PRECIPITATION TREATMENT

Economically, the conventional precipitation treatment is becoming less and less attractive with each increase in the cost of water, since the treated effluent is not normally of sufficiently high quality to permit recycling. Furthermore in the U.K. it is common practice to make charges for receiving the treated effluent, the charge depending on both the volume of effluent and upon the degree of contamination. Thus industry has frequently to bear the double cost of purchasing water and of discharging the water after use. The costs vary considerably with the region, but typically the total cost has increased five-fold between 1968 and 1974. It is unlikely that it has yet reached a plateau. Typical costs for the purchase of water and for the discharge of treated industrial effluent are shown in Table 4.⁶ This table ignores the cost of effluent treatment, and reflects solely the tolls levied for accepting the effluent, usually into public authority sewers. It follows that there is now a strong and growing incentive to adopt practices which facilitate water recycling within the works. The cost of water for rinsing work after pickling or plating is a significant proportion of the total processing cost. In fact the savings which could be made from recycling water are of greater significance than monies

which might accrue from the recovery of metal from effluents, bearing in mind the probable cost of a recovery operation. Obviously a process which enables water to be recycled and metals to be recovered is doubly attractive.

AVAILABLE TREATMENT PROCESSES

The methods of effluent treatment available to the non-ferrous metals industry include:

- (a) Precipitation
- (b) Ion-exchange
- (c) Electrolysis
- (d) Crystallization
- (e) Evaporation/distillation
- (f) Cementation
- (g) Reverse osmosis
- (h) Electrolysis
- (i) Adsorption
- (j) Liquid/liquid extraction

Precipitation, as outlined above is most widely used and it is applied mainly to the treatment of combined waste waters arising from various pickling or finishing operations. However, it has been applied to the treatment of waste water at source, i.e. at a single rinse tank, in the technique of so-called "integrated treatment". The metal hydroxide produced is then of simpler composition which may make recovery more attractive, but the main claim for the process is that the rinse water may be recycled. In practice, the build-up of chemicals in the rinse water requires a bleed-off and make-up with clean water which is stated to be about 20% of the volume circulating.⁷

Electrolysis is widely used for regenerating pickling solutions used for treating copper, but dilution is too great for efficient electrolytic recovery of metals from rinse waters. While it is possible to obtain increased cathode efficiency by employing "fluidized bed" electrodes,⁸ it is doubtful whether metals could be removed down to a level acceptable for effluent discharge. Cementation suffers from the same drawback. It is feasible to recover copper from dilute waste waters by displacement using iron scrap, but the resulting effluent still contains several ppm of copper in solution,⁹ and the substitution of iron sulphate for copper sulphate does not assist in making the water suitable for recycling.

Crystallization and evaporation or distillation are more suited to the recovery of metals from concentrated exhausted pickling solutions than from dilute rinse waters; similarly liquid/liquid extraction is more applicable to fairly concentrated solutions. In fact in reviewing the available processes only ion-exchange and reverse osmosis appear to possess the required characteristics of enabling a high proportion of water to be recycled and preventing loss of metal with an effluent stream. Ion-exchange is already being used in the electroplating industry and at least one plant is now in operation treating the effluent from a copper semi-fabricating works. Reverse osmosis as applied to effluent treatment is less well developed, but on first consideration it appears to

Table 4. Typical U.K. water costs

Unit	1968			1974		
	Purchase	Discharge	Total	Purchase	Discharge	Total
pence/1000 gallons	4.0	1.6	5.6	22	8	30
pence/m ³	0.88	0.35	1.23	4.84	1.76	6.60

have the attraction over ion-exchange in being basically simpler and continuous, with no regeneration cycle. There are, however, doubts about the life of membranes under the conditions of low pH operating in effluent treatment plants dealing with waste waters arising from pickling operations. These doubts are unlikely to be resolved until long-term pilot scale tests have been made. Assuming a good life for the membranes, costs would appear to be similar to ion-exchange treatments. So far experiments seem to have been confined to the recycling of nickel plating rinse waters where conditions for the membranes are possibly less onerous.

PRACTICAL APPLICATION OF ION-EXCHANGE

A closed circuit ion-exchange treatment plant for pickling effluents has recently been described by Camenisch.¹⁰ It is illustrated diagrammatically in Fig. 6. Rinse waters are collected from nine pickling areas and suspended solids are removed in a settling tank which is monitored to ensure that concentrated pickle does not accidentally enter the regenerating system. Before entering the ion-exchange units, the rinse water is filtered in a multi-bed filter containing layers of sand and activated carbon. This removes oil, grease, or surfactants which could poison the resins. The filter is cleaned weekly by back washing. Both cation and anion exchange columns are used yielding demineralised water which is fed back via a storage tank to the pickling plants. Twin sets of ion-exchange columns are used and when one set is exhausted there is an automatic change over to the second set.

Regeneration takes place about every 12 hr and the regeneration cycle takes about 2 hr. The regeneration liquors are neutralised to precipitate the metal hydroxides, which, after settling, are filtered to produce a filter cake with about 30% solids. The filter water is processed through a small cation exchange column to remove the last traces of copper and zinc before discharge to the sewer.

This plant has a capacity of 80 m³/hr and it enables more than 95% of the water to be recirculated. The capital cost (1972) was about 1½ million Swiss Francs, excluding all the drainage work, most of which would be required for any effluent treatment system. The operating costs of this plant are shown in Table V from which it can be seen that the effective cost of the recycled water is about 0.64 Sw.Fr. per m³. (about 10 pence/m³). The author points out that this is still very much higher than the current cost of industrial water in the area (about 0.10 Sw.Fr./m³), but presumably it would be necessary to treat the effluent in any case in order to reach an acceptable standard for discharge and the cost of this treatment has to be added. The cost of conventional neutralization is in the region of 5–8 pence/m³ in the U.K., equivalent when adjustments are made for exchange rates to say 0.4 Sw.Fr. Thus the cost of water and of conventional effluent treatment is approaching that of the recycled water cost. If, as in some cases, a charge has also to be paid for discharging treated effluent, it may be seen that the ion-exchange plant is already offering an effluent treatment comparable in cost, if not cheaper than the conventional precipitation process.

Thus, although the high initial capital cost is a deterrent, long term economics appear to be changing in favour of ion-exchange because of the attraction of water recycling and the system would seem to be a strong contender for new installations.

NEW PICKLING FORMULATIONS

Changes in effluent treatment in the copper industry are being accompanied by modifications to pickling practice which simplify the treatment of rinse waters and also facilitate the electrolytic regeneration of the pickling solutions. Although dilute sulphuric acid is the common pickling agent, for some purposes it is desirable to use an oxidising solution. Sulphuric acid-dichromate pickle, is the traditional solution for brass and a range of copper alloys. The presence of the chromate ion complicates both

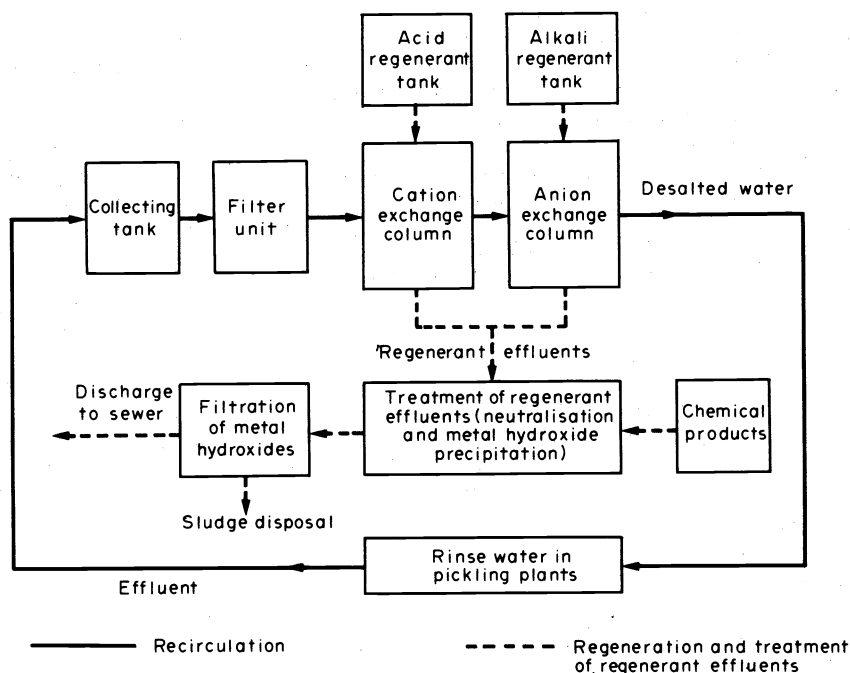


Fig. 6. Closed circuit water system in the ion-exchange treatment of pickling effluents.

Table 5. Operating cost of ion-exchange plant in Sfr. 1973

	Cost	Economics
Direct costs (including labour, maintenance, power)	102,130.00	
Calculated depreciation	163,170.00	
Total factory costs	265,300.00	
Economics 318,000 m ³ water copper recovered		31,800.00 28,200.00 60,000.00
Effective cost Cost of water per m ³	205,300.00 .64	

electrolytic regeneration of the pickling acid and also the treatment of the effluent. Over the past 5 yr progress has been made in substituting hydrogen peroxide as the oxidising agent,¹¹ which avoids the effluent treatment complication and does not interfere with the electrolytic recovery of copper from the pickle solution.¹² Stabilized hydrogen peroxide is now available capable of operating in pickling baths and a chemical efficiency of 80% is stated to be achieved. Recommended concentrations vary widely from as little as 2 g/l of 35% hydrogen peroxide to 30 g/l depending on the alloy being pickled, though there is a danger from the higher concentrations in that the oxygen bubbles generated can carry acid droplets into the atmosphere.

The appearance of work pickled in hydrogen peroxide containing solutions is different from that pickled with chromic acid as the oxidising agent and customer reaction may be a deterrent to the wider adoption of this newer pickling method. On the other hand, it is claimed that the chromate conversion coating resulting from the dichromate pickles can lead to tool wear in drawing brass wire.¹³ Some operators have also reported difficulty in obtaining a satisfactorily clean finish on some copper alloys. This may be a question of optimising the pickling conditions and more work is obviously required.

The efficiency of the pickling solution decreases if the copper content builds up and there is an increasing tendency to cause staining of brass. Build up of zinc in the pickle has little or no effect. By cycling the pickle through and electrolytic cell the copper can be plated out and sulphuric acid regenerated. Drag-out of pickle solution and make up results in an equilibrium value being attained for the zinc concentration. Thus it is possible to keep the pickling solution working almost indefinitely with only fresh additions of acid to compensate for drag-out.

As a result of these developments significant progress is being made towards closed systems with very little waste

for disposal. In a few plants, the possibility has already been demonstrated. The cost of changes will undoubtedly delay wide application of the newer methods, especially in the present economic climate, but increasing charges for water, problems of effluent and waste disposal, and more stringent effluent purity standards are all tending to make the closed cycle concept more attractive.

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