MEASURES TAKEN AGAINST WATER POLLUTION IN BASIC NON-FERROUS METAL INDUSTRIES

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ABSTRACT

Waste water purification is shown to be an important field of environmental hygiene for non-ferrous metal industries. Hydrometallurgy becomes of greater importance for metal production and refining. Quality standards for drinking water and rivers require a minimum of some harmful impurities, e.g. metal compounds.

The unit operations of hydrometallurgy technologically parallel the methods of effluent treatment in the non-ferrous metal industries. Examples are given which show recent developments and ways of relieving lower degrees of waste water pollution: (1) Increase in the use of salt solutions for producing magnesium; (2) Measures for the prevention of air pollution during aluminium electrolyses cause new effluent problems to arise; (3) Wet or dry gas cleaning in the case of salt cover furnaces at aluminium re-melting plants; (4) Change in a process for copper cementation—copper(I) chloride as an intermediate product of metal recovery; (5) Ion exchangers as concentration steps for purifying waste water containing non-ferrous metals; (6) Waste water purification at an ISP plant; (7) Utilization of leaching residues from zinc electrolysis plants; (8) Use of waste lime for hydrometallurgical processes; (9) Recovery of special metals by means of ion exchangers; (10) Recovery of service water as a valuable product in the purification of waste water in basic non-ferrous metal industries.

Nevertheless, some unsolved problems need better technical processes to reduce unfavourable biological effects produced by low concentrations of metal salts. Future developments in non-ferrous metal works have to examine the water economy conditions closely in order to meet the requirements for a higher metal yield and a better water purification.

INTRODUCTION

The prevention of water pollution is part of the more comprehensive science of environmental hygiene. Viewing all production processes as a whole, the extent as well as the direct and indirect cost of the prevention of water pollution is greater than for any other sector (*Figure 1*).

With regard to the basic non-ferrous metal industry section, it is of particular importance to have a clear mind on the consequences of purifying waste water on the other sections of environmental hygiene. All that can be achieved by purifying processes of any kind is to make the material flow in the direction desired; thus, for example, solids can be eliminated, or metal

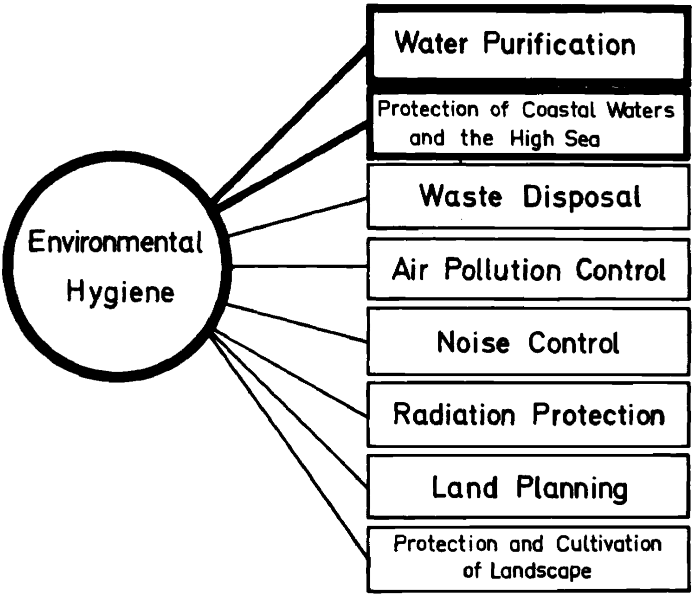


Figure 1. Water purification as a part of environmental hygiene

ions precipitated from solutions by means of chemical and electrolytic processes; furthermore, they can be cemented or concentrated by ion exchangers. If it is impossible to recover the metal directly or in the form of a starting material for metal production, the problems will simply crop up somewhere else in the field of environmental hygiene. For example, the waste water will be clarified, it is true, but the deposition of precipitated sludges can have long-term disadvantages with regard to water supply. For the basic non-ferrous metal industries a modification of the scheme is necessary. (*Figure 2*).

To begin with, the high proportion of thermal processes for recovering non-ferrous metals as compared with hydrometallurgical processes requires higher expenditure for the prevention of air pollution. Furthermore, the prevention of water pollution and the other sectors are interdependent in several respects. Generally speaking, increasing demands have to be met in the prevention of water pollution with every step in the fabrication of non-ferrous metals and their alloys up to the finishing stage.

The Importance of Non-Ferrous Metals to the Economy and to Waste Water Techniques

The increase in the production of non-ferrous metals, their extensive use in all technical fields as well as in every household, and the fact that certain concentrations of many non-ferrous metal compounds can have a toxic effect upon the biological entities in water, are indicators of the increasing importance of measures against water pollution for the non-ferrous metal industries. Almost two thirds of all native elements are metals. In 1969, the whole primary non-ferrous metal production amounted to about 5 per cent

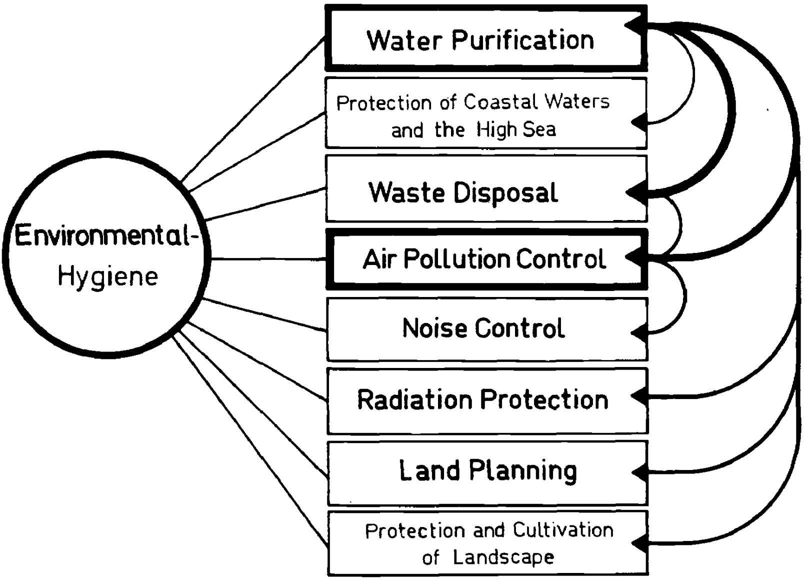


Figure 2. Non-ferrous metal works and environmental hygiene

of the world's crude steel in tonnage, but came near to the material value (*Figure 3*). However, these facts give no idea of the real importance of the basic non-ferrous metal industries and their measures against water pollution. Non-ferrous metal plants are of far greater importance to many sewage

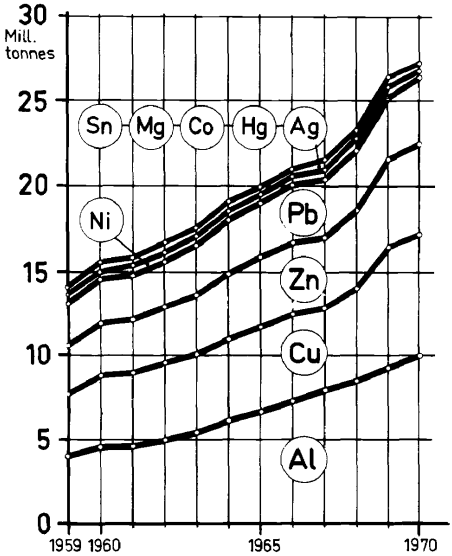


Figure 3. World production of primary non-ferrous metals, 1959–1970

treatment plants and public waters than are bigger plants for the production and treatment of steel.

The last two decades have seen the use of a large number of special metals and research into the specific properties of materials belonging to a large group of rare metals. The technical and economic advantages of utilizing differentiated properties of non-ferrous metals will bring the minor metals of today into common use. Elements, hitherto seldom used, will soon find technical application. Thus, waste water techniques will have to cope with new problems and new tasks.

In addition to serving the important purpose of being a process for the recovery of conventional non-ferrous metals, hydrometallurgy[1] has increasingly come to be of even greater importance with regard to special metals (*Figure 4*). At the same time, the processes for purifying waste water, operated on the same principles, have equally been improved.

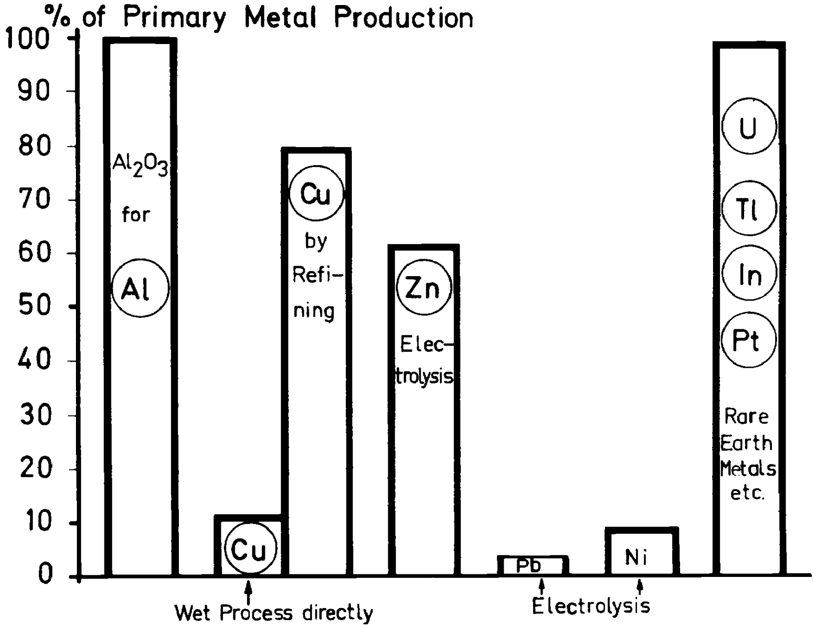


Figure 4. Hydrometallurgy as a basis for metal production and refining

GENERAL ASPECTS OF WASTE WATER PURIFICATION IN BASIC NON-FERROUS METAL INDUSTRIES

So far, legislators, lawyers, chemists, engineers, and biologists have hardly thought of the task of preventing water pollution in terms of aiming at a minimum of undesirable effects upon every one of the sectors of environmental hygiene. The difficulties of specifying and implementing quality standards for harmful impurities contained in drinking water and in waste water have already become so great that only recommendations have been put forward. *Table 1* shows recommendations for different qualities of water with regard to their metal contents.

Table 1. Standards for drinking water and rules for sewage

	Drinking water European standards WHO	*Industrial effluent*	
		German rules for charging in the city sewerage	*'Normal Rules' after treatment (Prof. Husmann)*
pH	7–8.5	6.5–9.5	6.5–9.0
Fe^{2+}	0.1 mg/l	(no limit)	2 mg/l
Mn^{2+}	0.1 mg/l	——	1 mg/l
Cu^{2+}	1.5 mg/l	3 mg/l	1 mg/l
Ni^{2+}	——	5 mg/l	3 mg/l
Zn^{2+}	max. 5 mg/l	5 mg/l	3 mg/l
Pb^{2+}	max. 0.1 mg/l	——	1 mg/l
As^{3+}	max. 0.2 mg/l	——	——
Cr^{6+}	max. 0.05 mg/l	0.5 mg/l	——
Cr(total)	——	4 mg/l	2 mg/l
Cd^{2+}	max. 0.05 mg/l	3 mg/l	3 mg/l
F$^-$	max. 1.5 mg/l	10 mg/l	2 mg/l
CN$^-$	max. 0.01 mg/l	1 mg/l	0.1 mg/l

The extension of the prevention of water pollution within the framework of comprehensive environmental hygiene

On this basis, inevitable in the long run, the basic non-ferrous metal industries will be required to pay more attention to the following possibilities:

Recovery of metals or metal compounds.

Processes for decreasing the amount of water required (recirculation, regeneration, recooling, etc.). The prospect of saving water is as important as the necessity of purifying waste water.

The use of heating methods even in a protective gas atmosphere or in a vacuum, with pickling being restricted.

Processes for decreasing metal losses in washing water and in waste water (cascade washing technique, spraying technique, use of ion exchangers, general improvement in pickling techniques).

Investigation into the utilization at plant level of metal-bearing solutions, sludges, and other residues from water purification plants. Depending upon the circumstances, the sale of the material or the treatment at a central plant can be more economical.

The location of new non-ferrous metal plants should be examined, in particular, with regard to the proper handling of waste water.

To sum up, a higher metal yield must be obtained. The material conversions required necessarily result in products that cannot be utilized any further; for example, these products may take the form of additional amounts of chloride or sulphate which will have to be discharged into the nearest river.

Technological parallels between hydrometallurgy and waste water purification

Hydrometallurgical processes for the production of non-ferrous metals[2, 3]

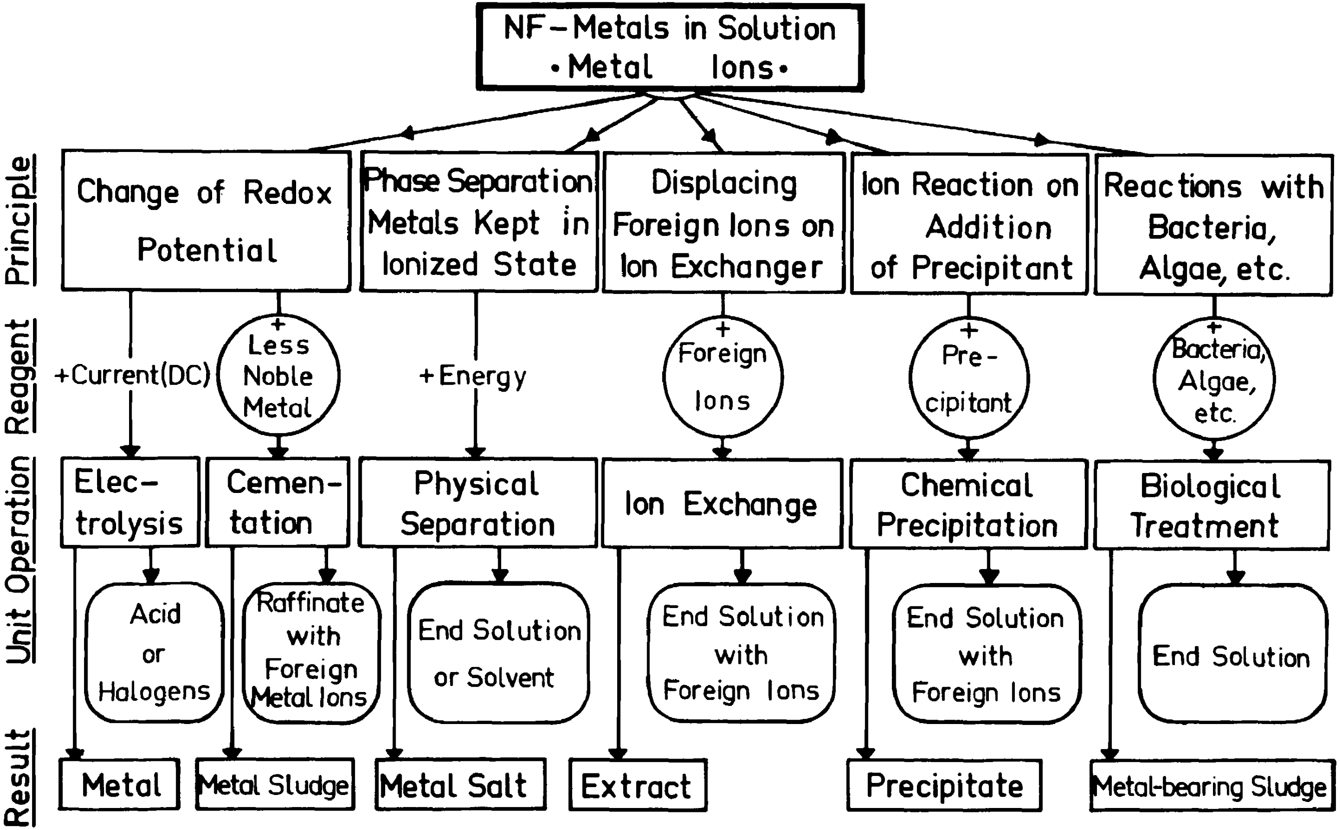


Figure 5. Unit operations in hydrometallurgy and waste water treatment in non-ferrous metal works

make use of the same physical and chemical processes as are of interest to the treatment of waste water at non-ferrous metal plants. *Figure 5* shows a survey of those methods and their effect on the flow of material.

Referring to the hydrometallurgical parallels is material in the sense that an improved technology of water purification can effect the recovery of those valuable non-ferrous metals except for minimum concentrations.

Hence, the economy of the processes competes with the cost of removing any kind of metal-bearing residue by disposal at selected sites.

EXAMPLES OF NON-FERROUS METAL EXTRACTION FROM WATER

The extensiveness of the field of effluent treatment in the non-ferrous metal industry must place certain restrictions upon the scope of this review. The following examples show recent developments and tendencies in the conversion of materials with regard to effecting a lower degree of waste water pollution:

(1) Increased use of salt solutions for producing magnesium

Magnesium, a special metal during the first third of this century, became a widely used metal about 35 years ago. Saline solutions and sea water represent inexhaustible sources of raw materials. The world's highest production of 232 000 tons in 1943[4, 5] will be equalled again in 1970 and in 1971.

From a point of view of effluent treatment, the increase in the use of saline solutions is valuable. The most important European producer, Norsk Hydro AS in Heroya, Norway (about 40 000 tons in 1970), makes use of increasing amounts of salt solutions, imported from the Federal Republic of West Germany, in addition to sea water.

The enormous amount of chlorine, required by the chemical industries—for instance, 1.6 million tons in the Federal Republic of West Germany in 1969—lends support to a project to erect in Northern Germany a new magnesium electrolysis plant based on using saline solutions. Thus, inland waters can be relieved of the contained non-ferrous metal salts and chlorides.

(2) Measures for the prevention of air pollution during aluminium electrolysis cause new waste water problems to arise

European aluminium plants have to prevent any harmful effect by means of gaseous fluorine compounds[6]. Therefore, they have to subject the waste gases from the electrolysis furnaces to wet cleaning. Owing to the considerable increase in today's productive capacity in Europe, the two processes used are those for purifying potroom air and washing concentrated waste gases from enclosed furnaces (*Table 2*)[7–9]. In both washing processes waste water is obtained from which utilizable sludges and clear water with a low content of fluoride are produced at a purification plant. The sludges are of interest in that there is a possibility that their fluorides can be converted into usable compounds such as Na_3AlF_6, NaF, AlF_3 or CaF_2. The precipitation of the washing water is effected by controlled additions of NaOH and $Al(OH)_3$, $Ca(OH)_2$ also being used at some plants. Besides

$Al_2(SO_4)_3$, $Fe_2(SO_4)_3$—which is cheaper—or treated red mud from the production of alumina may be used as flocculating agents. It is conventional for sedimentation aids to be used.

Table 2. Fume purification processes in primary aluminium reduction plants

		Potroom gas cleaning	*Furnace gas extraction and cleaning*
F Input by flux, kg F/ton Al		35–40	35–40
Furnace emission, kg F/ton Al	gaseous	10–15	10–15
	in dust	7–10	7–10
Waste gas, m³/ton Al		2 200 000	150 000–200 000
Washing water (to re-use), m³/ton Al		200	<20
Total F emission (gaseous) after cleaning, kg F/ton Al		0.5–1.2	0.7–1.5
Total F emission (in dust) kg F/ton Al		2– 6	3– 7

The different measures for the prevention of water and air pollution in the case of new plants built for aluminium electrolysis are a case in point of the individual character of the solution required according to the circumstances of the problem. At the oldest European aluminium plant, located in Rheinfelden in the Federal Republic of West Germany[10], different systems are used for Söderberg furnaces and furnaces equipped with baked electrodes. The concentrated waste gases from the enclosed Söderberg furnaces are subjected to dust separation by means of cyclone separators and electrostatic separators; subsequently, they are conveyed into scrubbing towers

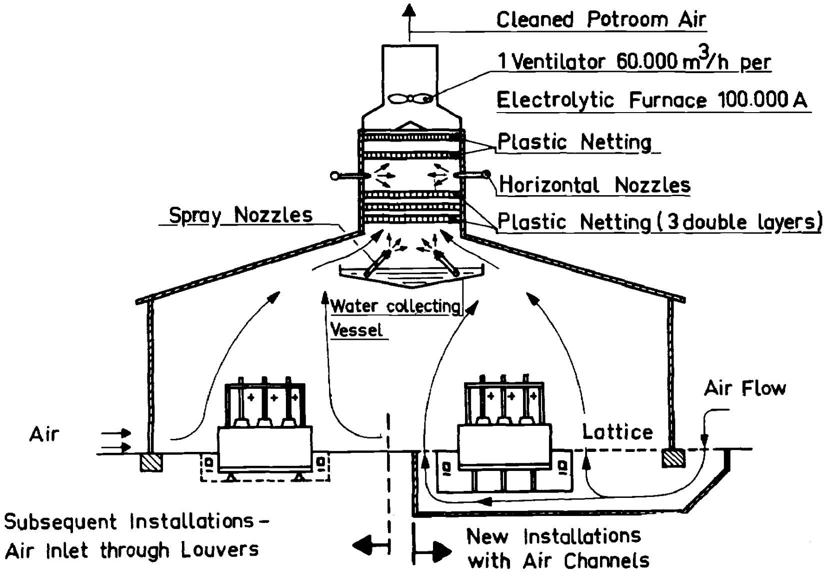


Figure 6. Potroom gas cleaning in aluminium reduction plants (Alusuisse system)

where over 99 per cent of the HF content of the gas of about 500 mg/m^3 are extracted by means of recirculation washing. Hydrofluoric acid, with a content of about 3 per cent, is removed, and worked up by reaction with NaOH and AL(OH)$_3$ into cryolite (Na$_3$AlF$_6$). After drying, this salt is fed back to the electrolysis as a flux.

The waste gases from the furnaces equipped with baked electrodes are subjected to potroom air purification (*Figure 6*).

The large amounts of washing water (200 m^3 per ton of Al), containing about 70 mg per litre of F in solution, are conveyed into the Rhine river.

The amounts of F contained in the Rhine—about 0.20 mg per litre—are too low by drinking water standards, so the content is increased to 0.22 mg per litre by means of these additions. At about 0.30 to 0.35 mg per litre, at the Dutch-German border, the F content is only one third of the drinking water concentration intended. The authorities and the International Rhine Water Commission have shown great understanding towards the increase of the fluorine burden. Owing to the solubility of fluorspar (about 16 mg of CaF$_2$ per litre at summer temperatures), this also applies to technical precipitation processes producing final waste water of this concentration.

The Alusuisse potroom air purification process was improved for the benefit of the new plant at Gebr. Giulini GmbH at Ludwigshafen, which has been producing 22000 tons of aluminium since 1969, and at Leichtmetall-Gesellschaft in Essen, which will go into operation at the beginning of 1971 with a capacity of 84000 tons per year (this capacity is to be increased to 126000, and eventually, to 168000 tons per year). At Ludwigshafen, a neutralization and thickening plant for purifying washing water is used subsequently. This plant allows a choice of using Ca(OH)$_2$ or NaOH and ensures a discharge of clear water within a pH range of 6 to 8. Treatment of the sludge is planned.

At the Essen plant on the site of the former Krupp blast furnace plant, there is no sufficient water supply for continuous flow washing. Hence there is recirculation, with precipitation, neutralization, and sludge separation as intermediate stages.

At VAW's Rheinwerk (ultimate capacity: 140000 tons per year of Al in 1971) and at the Kaiser-Preussag electrolytic plant at Voerde at the mouth of the river Lippe (ultimate capacity of 140000 tons), the waste gases from the enclosed electrolytic furnaces are first subjected to a mechanical removal of the dust, then to multiple-stage washing. Rheinwerk's washing, precipitation, and thickening plant is said to guarantee such extremely low waste gas concentrations as about 1 mg/m^3. On the first furnace building being put into operation, the Kaiser-Preussag plant[11] is going to neutralize the washing water with lime and to convey the overflow from the thickener back into the gas scrubber (*Figure 7*). Vacuum filters remove the water contained in the material discharged from the thickener so that the value of the residual moisture is 50 to 70 per cent. The filter cake contains 70 to 80 per cent of CaF$_2$. The new aluminium electrolysis plants at Invergordon, Holyhead in Anglesey, and Lynemouth in Great Britain also use enclosed furnaces equipped with baked electrodes. The waste gases are washed[12]. So far, there has been no satisfactory solution to the problem of working up the sludge. As yet, no solutions have been found for some technological problems,

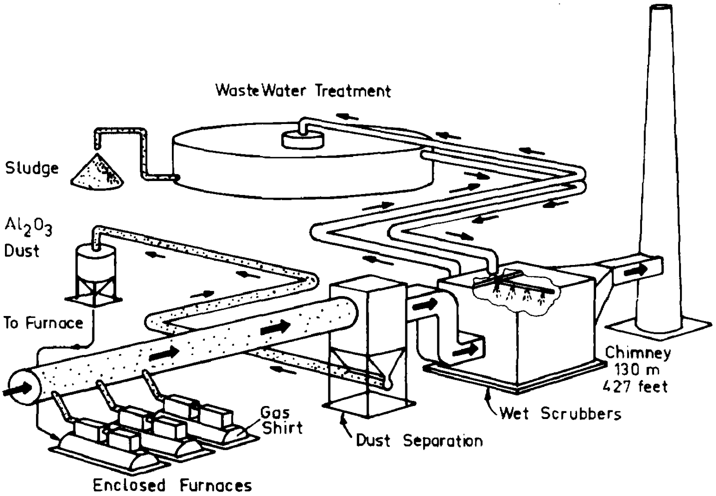


Figure 7. Gas purification by circulation (Kaiser- Preussag)

particularly with regard to the question of what minimum capacity would be economical. In view of a price of about 100 dollars per ton of F in the fluxes Na_3AlF_6 and AlF_3 required for electrolysis, there is a great incentive to recover the fluoride material. Thus, for example, the filter sludges from Rheinwerk, together with material from other electrolytic plants, are centrally worked up to F compounds at the Lippe plant. The dry purification process, developed by ALCAN, makes use of Al_2O_3, thus avoiding any addition of water for washing processes. On the other hand, the 95 per cent degree of separation that can be achieved is considered below the mark by the European authorities.

Wet or dry precipitation in the case of salt cover furnaces at aluminium re-melting plants

The removal of the dust arising from the furnaces for melting down aluminium scrap, where the metal is covered with molten salt (NaCl + KCl) for the purpose of preventing oxidation by air, is extremely difficult. In order to solve the problem, not only dry purification processes[13], but also washing processes were used. However, they merely transfer the problem of pollution from air to water. In practice, this requires both a stream large enough to take the salt burden and special measures for protecting installations against corrosion.

In the Federal Republic of West Germany, two commercial plants have been built. A pressure-drop washer, including a first stage scrubber, requires one m^3 of water for every 500 standard cubic metres of waste gas. Subsequent to intensive scrubbing, the second design is operated according to the condensation principle. 2500 to 3000 m^3 of waste gas are purified for every m^3 of water fed in. The washing water alkalified with NaOH also takes care of the HCl and the SO_2 in the waste gases from the furnace.

After the separation of the sludge the salt solutions are conveyed into the river.

The flow of material precipitated from the vapour of the molten salt into inland waters is not satisfactory. However, there are favourable conditions at remelting plants in coastal areas.

Progress in dry precipitation techniques[13] has led to merely local applicability of wet purification processes. The example goes to show that the basic non-ferrous metal industries are compelled by the difficult problems of environmental hygiene to try out processes which are going to be a burden to effluents.

(4) Change in a process for copper cementation—copper(I) chloride as an intermediate product of metal recovery

The well-tried process of copper cementation with iron can also be used for diluted solutions (0.3–3 g Cu/l) of mine waters and industrial waste water when iron powder is added. A special design, the discontinuous Kennecott cementator[14], makes it possible to reclaim copper down to residual contents of 2 to 10 mg/l. At Kennecott's Utah Copper Division, over 60000 tons per year of copper are produced by means of extraction from dumps and subsequent cementation in accordance with the new process. All cementation processes cause the problem of burdening the waste water to be transferred to the side of the baser metal, for example, from a Cu burden to an Fe burden. Precipitation methods for Fe after oxidation to Fe^{3+} are well known, but expensive. Duisburger Kupferhuette succeeded in extensively economizing in iron by means of lime precipitation from $CuCl$ to Cu_2O. The drum filter cake with an adhering moisture of about 40 per cent may be directly worked in the shaft furnace to blister copper containing precious metals.

Figure 8 shows the flow sheet of a plant designed for the production of 25000 tons per year[15]. In the first precipitating cascade, the cement copper added reduces the copper salts to Cu(I) compounds. The chloride content in the solutions precipitates the greater part of the copper content in the form of slightly soluble $CuCl$. Chloro complexes prevent complete precipitation. The subsequent drum cementation has the advantage of requiring stoichiometrically smaller amounts of scrap for the copper(I) salts. The cement copper separated is conveyed to the first precipitating cascade. The precipitating reactions of both cascades are automatically controlled via electric potential measurements.

The thickener overflow from the Cu_2O precipitating cascade is passed at a pH value of 7.5 to 8.0 through three pressure filters together with the washing water from the revolving filters. The economy of the process is favoured by continuous reductions in the price of CaO. Thanks to advanced burning techniques, lime is considerable cheaper today than scrap iron, which is exactly the opposite of the truth 35 years ago.

As in the case of almost all technical and biological reactions, the chloride balance of the process causes the chlorides to be completely conveyed into the filtered waste water.

(5) Ion exchangers as concentration steps for purifying waste water containing non-ferrous metals

At present-day standards of technology, and in view of the quality of exchange resins, ion exchange often represents a useful as well as an

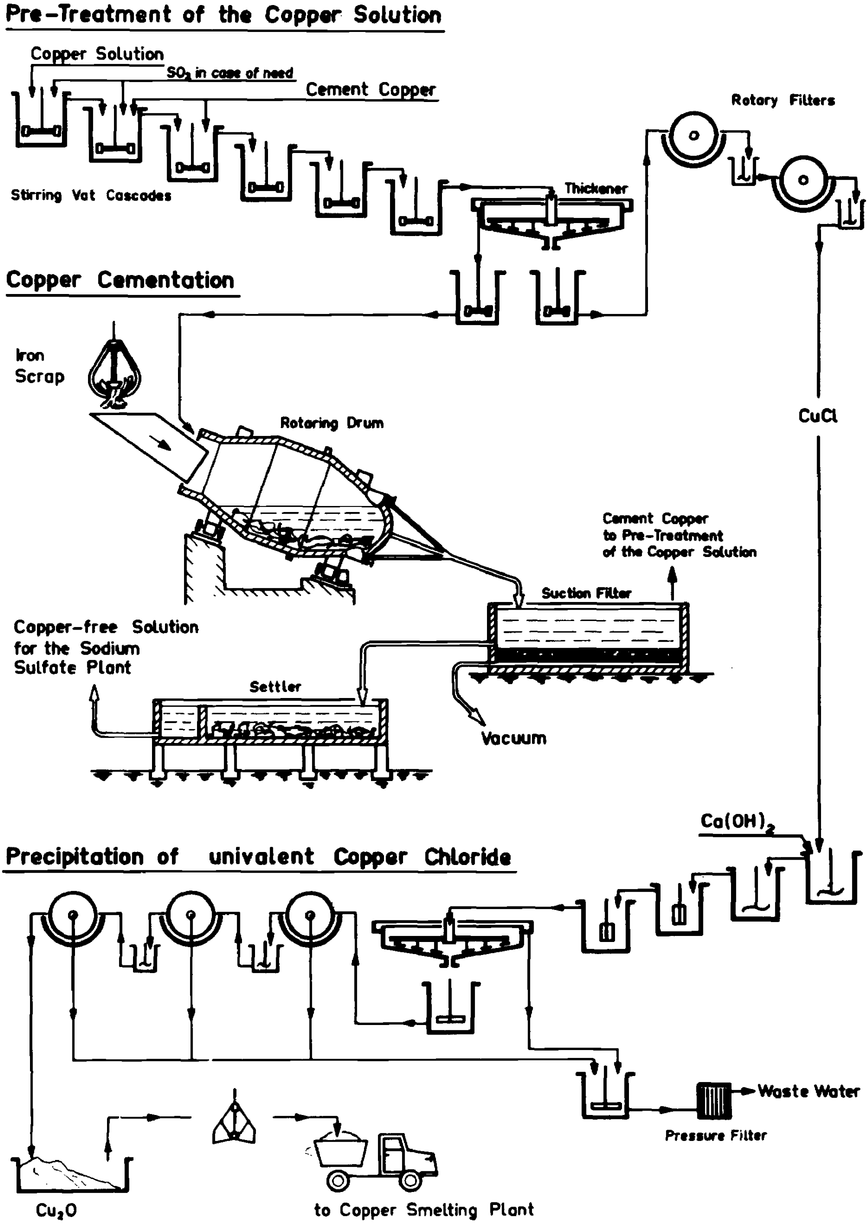
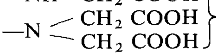


Figure 8. Cuprous oxide production from copper solutions

economical process for separating non-ferrous metals from waste water. Since, as a rule, the effluent obtained by re-extracting the saturated exchange resin produces enriched concentrates of the metals, further working up for recovery of the metals is made possible.[16]

It is imperative that a suitable cation-exchange resin should be selected seeing that it is required to stand up to constant changes in chemical, osmotic, and mechanical stresses. Often, it is preferable for the ion exchanger to have selective properties for the non-ferrous metals so that, in particular, it will effect stronger bonds with heavy metals than with alkaline earth metals and alkali metals, respectively. As is shown in *Table 3* cation exchangers can be divided, depending on the kind of fixed exchanging groups, into the strongly acidic type, the weakly acidic type, and the type that combines by complexing.

Table 3. Cation-exchange resins

Fixing groups	
$—SO_3H$	strong acid
$—COOH$	weak acid
$—NH—CH_2\ COOH$	chelating resins
 $—N\begin{matrix} CH_2\ COOH \\ CH_2\ COOH \end{matrix}$	

Order of bonding, weak acid resins, low selectivity:

$Cu > Pb > Zn > Ni > Cd$

Order of bonding, for complex-forming resins, strong selectivity, e.g. Lewatit Resin CA 9207

$Cu^{2+} > In^{3+} > Fe^{3+} > Ni^{2+} > Ag^{+} > Co/Zn > Fe^{2+} > Cd^{2+} > Tl^{+}$

alkali metals ← alkaline–earth metals ←

For the most part, the starting form of the resin for the absorption of non-ferrous metals from waste water is the protonated or Na salt form.

The resins differ above all with regard to bonding strength for the H ions as well as for the metal ions, i.e. in practice, with regard to the pH working range and the capacity to fix the metals by ion exchange with equal or different strength. This selective capacity is present in weakly acid resins with COOH groups, and it is far stronger in such complex-forming resins with aminocarbonic acid groups (chelating resins). *Table 3* shows a 'bonding series' for both types of resin in order of succession for metals with decreasing strength. In practice, this means that the metals which are more firmly fixed will be more enriched than the metals which are less firmly bound.

For example, it is not necessary, as a rule, in the discharge of waste water to remove the alkaline earth and alkaline ions as well. In this case, it is useful and economic to choose the weakly acidic, selective ion exchangers. Non-ferrous metal ions are certain to be removed from the waste water down to less than 1 mg/l and to be enriched in the resin or in the eluted extract, respectively; but higher contents of, for example, Ca ions pass through the resin column without interfering.

Full economical use is made of the exchange capacity which amounts to about 2.0 to 2.5 gram equivalents (val) per litre of resin, corresponding, for example, to 60 to 75 g of Ni, so that the non-ferrous metal is separated.

(6) Wase water purification at an imperial smelting furnace plant

The zinc and lead recovery process of Imperial Smelting Corporation Ltd. has been made use of on a world-wide scale within a decade of the initial installation at Swansea Vale, Wales, in 1960[17]. The capacity of the 13 plants, constructed or under construction, amounts at the moment to about 20 per cent of the world's zinc production. Although the thermal IS process, particularly well suited for zinc-lead complex ores, does not directly produce waste water containing basic non-ferrous metals, extensive measures against water pollution have to be taken at the subsidiary plants.

The specific amount of water required amounts to 80 to 100 m^3 per ton of Zn + Pb produced, inclusive of the production of sulphuric acid at a preceding roasting plant. Thus the amount is higher than that required at blast furnace plants, where 25 to 70 m^3 are required for every ton of pig iron produced, inclusive of blast furnace gas washing. In *Figure 9*, which shows the flow sheet of the process, the points at which there is consumption of water are particularly marked. No problems with regard to waste water technology are posed by the cooling water from sulphuric acid condensation, from shaft furnace cooling, and from lead cooling gutters. Here, there are three kinds of water added for recirculation: completely desalted water for the blast tuyeres, softened water for cooling, and town water for H_2SO_4 condensation.

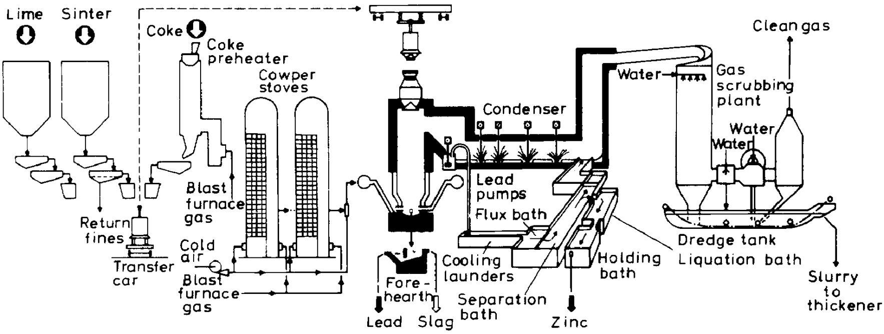


Figure 9. IS Shaft Furnace Process and its waste water points. Water requirements: 1, washer for waste gas from coke preheaters; 2, Venturi scrubbers for hot coke dust (850–900°C); 3, water jackets sprayed with soft water; 4, Tuyeres cooling with demineralized water; 5, soft water for cooling launders; 6, gas washing equipment (washing tower, disintegrator)

The water is burdened with dust and soluble compounds at the following points:

(A) Scrubber for the exit gas from the preheater for the coke;
(B) Venturi scrubber for precipitating the dust from the coke discharge (850–900°C);
(C) furnace gas washing with an injection tower, a disintegrator, and a subsequent separator;
(D) Venturi scrubber for extracting the dust from the room of the melting shop.

The high dust content in the furnace gas of about 35 g per standard cubic metre is decreased in the purified gas to less than 40 mg/m^3. For operating points A, B, and C, water is a purifying agent and a vehicle for conveyance. In a Sedimat thickener, 450 m^3/h of washing water, containing 500 to 1000 mg/l of solids, are clarified except for a residual content of 50 to 150 mg/l. The overflow is partially conveyed back to the Venturi scrubbers for room dust extraction (80 m^3/l), while the bulk of it is conveyed to the central clarifying plant (370 m^3/h).

The following operations serve the purpose of waste water purification in the precipitating vats preceding the final thickener:

(A) alkalization with Ca(OH) up to pH 10;
(B) chlorine oxidation in the case of cyanide contents of over 0.1 mg/l;
(C) neutralization to pH 6.5 to 7.5 by addition of the acid washing water from the wet electrical gas purification of the roasting gas purification;
(D) addition of $FeSO_4.7H_2O$ for precipitating traces of As compounds;
(E) addition of small amounts of flocculating agents.

The Sedimat thickener allows intensive mixing in the inner reaction chamber.

At a pH value of 6.5 to 8.5, the purified waste water contains:

below 4 mg/l of solids
3–5 (max.) mg/l of Zn (total)
0.5–1 (max.) mg/l of Pb (total)
0.3 (max.) mg/l of Cd (total)
0.5–1 (max.) mg/l of Cu (total)
1–2 (max.) mg/l of Fe (total)
0.02–0.1 (max.) mg/l of CN

Chlorine oxidation of the cyanide was carried out at the IS plant belonging to the firm of Berzelius Metallhuetten GmbH in West Germany[17] in the years immediately after the plant was put into operation in 1965. It was found that, on the basis of optimum operating conditions and a furnace capacity of about 100000 tons per year of Zn + Pb, the CN content in furnace gas washing was continuously decreasing. Traces amounting to 0.01 to 0.02 mg/l are still present.

The sludge–solids balance of the plant is a case in point of closed recirculation. While the coarse Pb–Zn sludge from the furnace gas washing can be directly added to the starting ore of the roasting plant from a settling pit, the so-called blue sludge of the first thickener must be conveyed from a drum filter to the sintering belt. The final thickener also produces sludges containing Pb and Zn; they are then conveyed to the roasting-sintering plant.

From a specific and from an absolute point of view, the amount of water required is high; hence, cost savings have to be effected by recirculating the different kinds of water inside the plant. It is only an optimum arrangement of the system that will secure low costs and the almost complete return of the metal-bearing sludges. The recirculation economy of water and non-ferrous metal sludge guarantees the success of measures against air and water pollution.

(7) Utilization of leaching residues from zinc electrolysis plants

Since the beginning of production at the first zinc electrolysis plant of

Anaconda in 1916, this branch of hydrometallurgy has reached, step by step, 60 per cent of primary zinc production.

In terms of waste water technology, this is a favourable recirculation process because the cell acid is used for leaching the roasted blende.

On account of the zinc ferrite content, the zinc content in the roasted blende cannot be completely extracted. The leaching residues obtained are a burden to water economy if they are dumped or discarded in pools.

The composition of the leaching residues varies considerably with the kind of zinc ore treated, with the kind of process used, and with the kind of sludges being fed from the electrolyte purification (*Table 4*).

The considerable metal contents have given rise to the development of different technical processes. However, the comprehensive task of utilizing all metal contents has held progress in research and process development[18, 19] to a minimum.

Table 4. Analysis of leaching residues from zinc electrolysis

	% min. max.		min. max.
Zn	10–25	Ag	100–1500 g/t 3– 50 oz./t
Fe	12–43	Co	30– 100 g/t
Mn	0.5– 2.5	As	0.05– 0.4 %
Pb	1– 8	Sb	0.04– 0.1 %
Cu	0.2– 2.5	S(total)	2– 12 %
Cd	0.1–0.5	S(as SO_4^{2-})	1.5– 8 %
In	0.03– 0.2	S(as S^{2-})	0.5– 4 %
Sn	0.01– 2.5	$CaO + SiO_2 + Al_2O_3$	10– 32 %

Hydrometallurgical processes such as:

intensive subsequent extraction;
leaching with concentrated sulphuric acid;
pressure leaching, also at high temperatures; and
the so-called jarosite process for producing a Pb–Ag concentrate

complete with thermal processes. Such thermal processes are:

charging the residues into shaft and reverberatory furnaces at lead and copper smelters, also into IS zinc shaft furnaces after sintering;
volatilization processes in the rotary kiln, in the sinter bed, in the fluidized bed roasting furnace, during suspension smelting, and during chlorinating volatilization;
sulphatizing and chlorinating roasting.

Owing to differences with regard to the composition of the leaching residues as well as with regard to location, only a few zinc electrolysis plants can make use of those thermal extraction processes, which do not pose problems to waste water technology. Those thermal plants must have a location which is favourable to transportation costs.

At the zinc electrolysis plant at Eitrheim, Norway, i.e. Det Norske Zinkkompani A/S[20], the jarosite process was developed for effecting a better non-ferrous metal yield. Jarosite, a mineral, whose composition is

$KFe(SO_4)_2.2Fe(OH)_3$, with K being exchangeable with Na^+ or NH_4^+, is obtained under certain precipitation conditions by means of hydrolysis of the iron compounds. Thus, it is possible to separate the iron, while, on the other hand, the acid economy of the electrolysis can be controlled by the basic iron sulphate. *Figure 10* shows a diagrammatic view of the extraction process.

At an H_2SO_4 concentration of 250 g/l and at temperatures of 95 to 106°C, 98 to 99 per cent of the Zn and 80 to 90 per cent of the Fe content in the leaching residues can be dissolved. The subsequent precipitation, at a maximum pH value of 1.5, is effected with ZnO being added in the form of roasted blende. During the precipitation of the iron, a loss of 5 to 8 per cent of the Zn cannot be avoided in the concentrated solutions.

A process for completely utilizing the leaching residues was developed by Duisburger Kupferhuette[21] and reported at the annual meeting of AIME in Washington in 1969. *Figure 11* shows the process which has been developed in the meantime. In the course of two parallel roasting processes, i.e. chlorinating roasting and sulphatizing roasting, all the non-ferrous metals are made extractable. Subsequent to percolation leaching, the iron oxide is obtained in the form of so-called purple ore which can be conveyed into the blast furnace after being sintered. For several years there has been a direct admixture of zinc leaching residues during the chlorinating roasting of the pyrites cinders containing Cu. Inclusive of 1970, about 200 000 tons of residues have been treated. Mention of a difficult metallurgical problem should not be omitted. Certain maximum concentrations of such non-ferrous metals as tin, antimony, and arsenic may not be exceeded in the purple ore if high-grade pig iron is to be produced in the blast furnace. For this reason, a

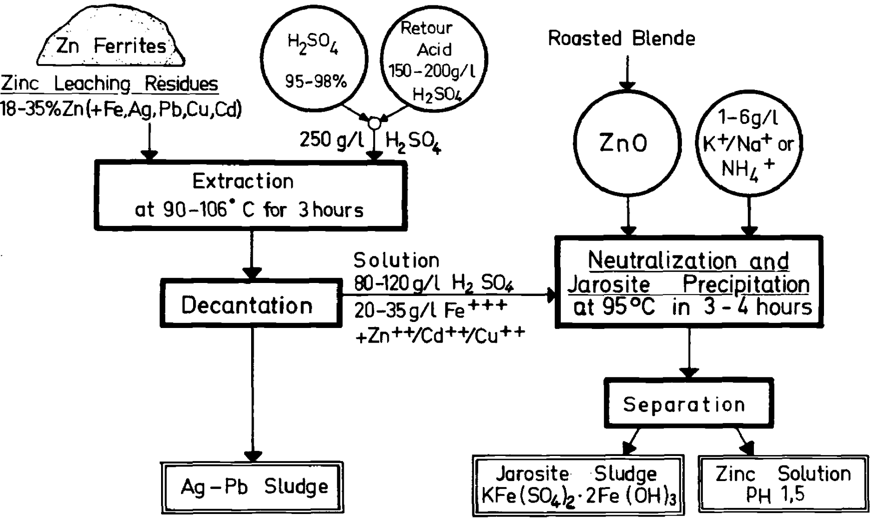


Figure 10. Flowsheet for Jarosite Process

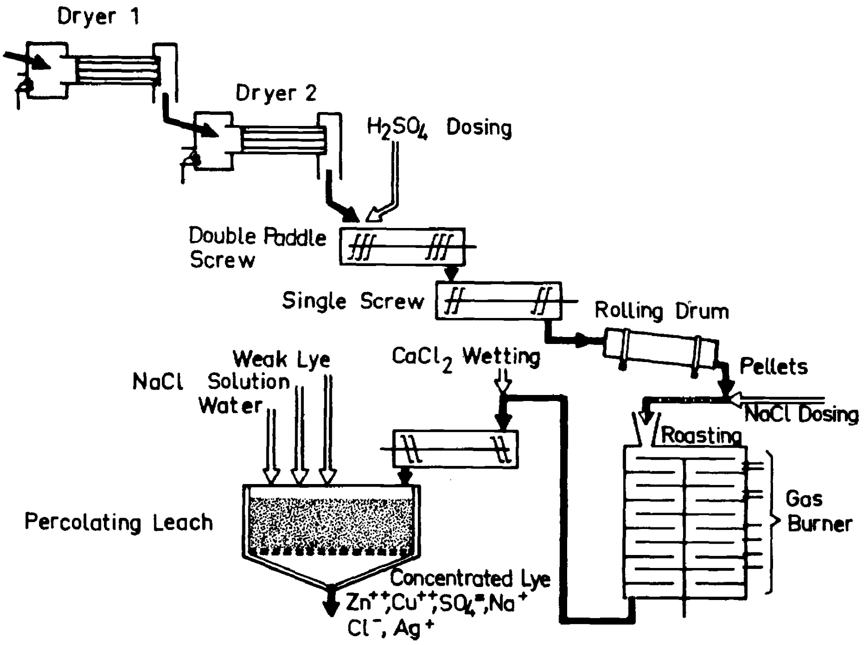


Figure 11. D.K. Process for working up zinc leaching residues

modification of the process for the exclusive treatment of zinc leaching residues has been developed. After admixing a specified amount of concentrated H_2SO_4 and maintaining a certain moisture level, it is possible to pelletize the material. Essential to the process is the favourable behaviour of the pellets in the 11-hearth furnace and during percolation leaching. In spite of the fine grain size of the residues, viz. over 90 per cent below 63 microns = 240 mesh, a gypsum crust can be built up if a $CaCl_2$ solution is added prior to leaching. Even after extracting more than 50 per cent of the volume, there will not be any formation of sludge. At the moment, there is no economical way of utilizing the gypsum–iron oxide residue.

Intensive researches are promising new developments in this interesting field for the next few years.

(8) Use of waste lime for hydrometallurgical processes

The cost of basic precipitation methods for metals is determined mainly by the amounts of alkali or alkaline earth which are stoichiometrically determined. Returns from the recovery of the non-ferrous metals or from the production of intermediates, such as oxides and carbonates, are determined by other factors in the metal markets regardless of the higher cost of production. Given this price–cost squeeze, the cost of precipitation has to be reduced. An interesting contribution to cost reduction is the use of waste lime as a carbonate or hydroxide sludge. Thus, a twofold contribution is made to the prevention of water pollution. On the one hand, there is no deposition of the waste lime which is available at a large number of chemical plants (produc-

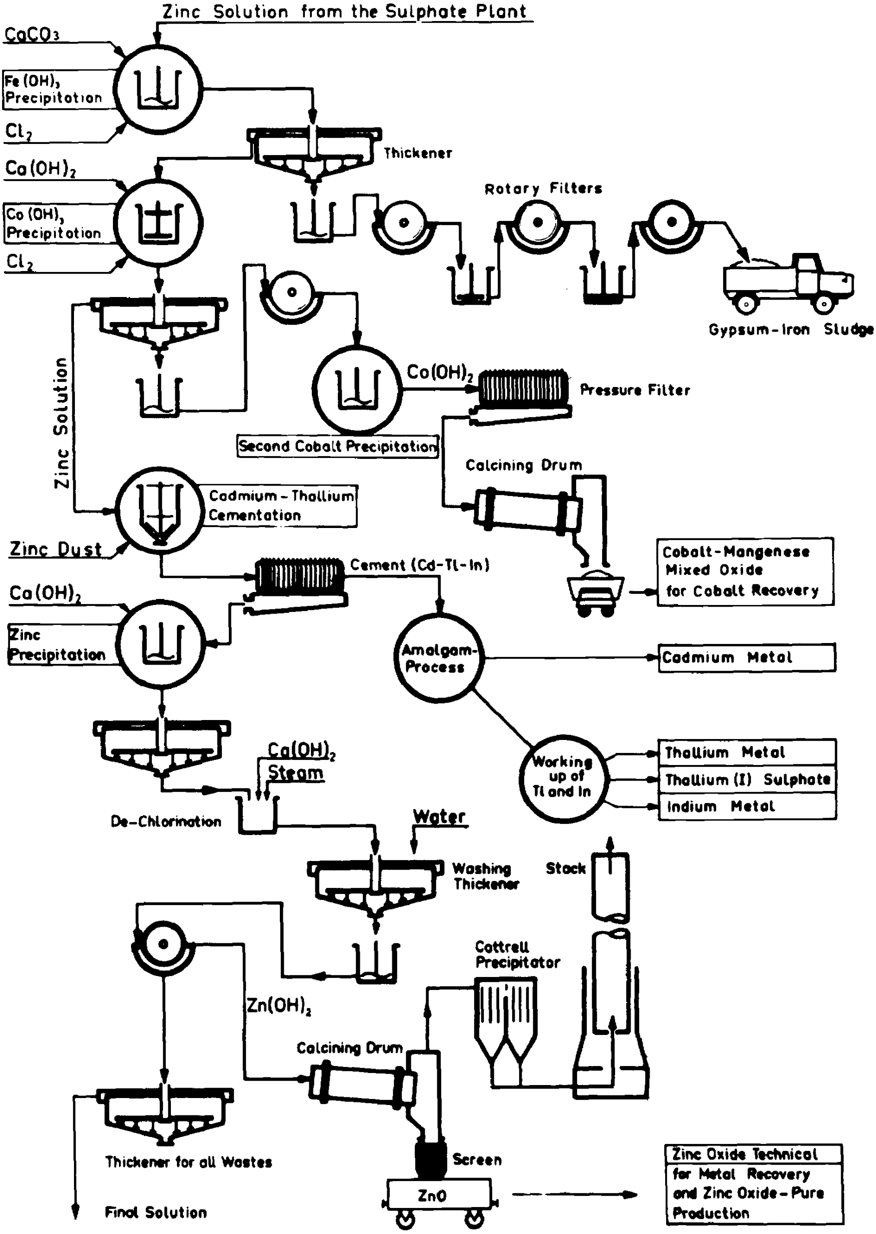


Figure 12. Treatment of zinc solutions

tion of acetylene on a carbide basis, coal-tar works, and organic chemistry). On the other hand, the recovery of non-ferrous metals from final solutions and waste water can be made more economical. Furthermore, it is important that the metal hydroxides and the basic metal salts should combine in the precipitation processes with a large number of organic impurities such as phenols, cresols, solids, etc.

These compounds, which are troublesome in terms of waste water technology even if low concentrations are present, are burnt during calcination for the purpose of recovering the non-ferrous metal oxides. *Figure 12* shows a flow sheet of the working up of the so-called final solutions from the chlorinating roasting of copper-bearing pyrites cinders.

The solutions with:

45–55 g/l Zn^{2+}
12–15 g/l Fe^{2+}
0.7–1.5 g/l Co^{2+}
0.1–0.2 g/l Ni^{2+}
1.0–2.0 g/l Mn^{2+}
150–180 g/l Cl^{-}
25–30 g/l $SO_4{}^{2-}$
150–200 ppm Cd
15–30 ppm Tl
5–15 ppm In

make it possible for annual production to reach:

50000–55000 tons of Zn
600–800 tons of Co
100–200 tons of Ni
70–100 tons of Cd
10–15 tons of Tl
2–4 tons of In.

Working up is effected in four stages:

(1) Oxidation of the Fe(II) compounds by means of chlorine. Precipitation with waste carbonate lime within a pH range of 2.8 to 3.0.

(2) Oxidation of the Co(II) and Mn(II) compounds by means of chlorine for separating Co–Ni. Precipitation of the Co(III) hydroxide by means of $Ca(OH)_2$ within a pH range of 4.0 to 4.2.

(3) Cementation of Cd, Tl, and In by means of zinc dust.

(4) Final precipitation of the zinc with the aid of waste lime ($Ca(OH)_2$) within a pH range of 6.5 to 7.0 with a subsequent precipitation of residual contents up to a pH value of 7.5 by means of burned lime.

The interesting point with regard to these precipitation stages is the high amount of waste lime (*Figure 13*). With the aid of today's advanced measuring and controlling techniques, it is possible for the zinc to be precipitated except for a residual content of 2 to 10 ppm (mg/l) of zinc in solution. The precipitating plant collects all leakages for re-use at a suitable point. The waste water is purified via a final thickener and discharged at a pH value of 7.5 to 7.8.

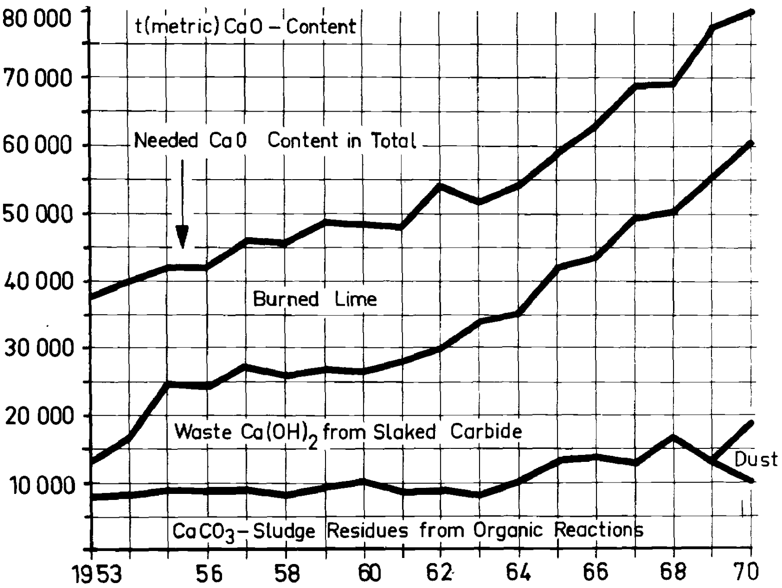


Figure 13. Limestone consumption in wet metallurgy of Zn and Co, 1953–1970 (Duisburger Kupferhuette)

(9) Recovery of special metals by means of ion exchangers

In the presence of higher manganese contents, the cobalt–nickel separation according to *Figure 12* requires large amounts of chlorine because of the formation of Mn(IV) and Mn(VII) compounds. This fact, as well as the desire to extract a larger fraction of the indium, has led to research in the field of ion-exchange technology. Today, after the great success in the production of uranium, intensive work is being done in this field in most of the industrial countries aiming to effect the hydrometallurgical recovery of special metals. For example, four large-scale ion exchangers for recovering cadmium via Amberlite IR 120 resin are in operation at the IS shaft furnace plants at Swansea Vale and at Avonmouth in the United Kingdom, and at Cockle Creek in Australia[22]. Thus, new vistas have opened up for the prevention of waste water pollution in the non-ferrous metal industries.

The selective properties mentioned above of the complex ion and chelate resins, for example, make it possible to bind the heavy metal cations, while the alkali and alkaline earth cations pass the resin column without any hindrance. In the field of zinc–cadmium hydrometallurgy, cadmium is enriched in the solution after lime precipitation, the pH value being 7.5. On account of the toxicity of the Cd compounds in the waste water, the possibility of selectively fixing Zn and Cd in a chelating resin column is a point of interest. Acid washing of the loaded resin produces a concentrated solution of 20 to 25 g/l of Zn + Cd. This intermediate product can be worked up in an economical manner. *Figure 14* shows the efficiency of the resin in separating indium from cadmium chloride solutions. For the purpose of commercially recovering the indium, a second In–Cd separation via the chelating resin is necessary[23]. The indium can be worked up electrolytically.

For the purpose of selectivity recovering the precious metals Au, Pt, Pd, Ir, Rh, Ru, and Os from extremely dilute solutions (1 microgram/l = 1 ppb), an anion-exchange resin with chelating groups is recommended in a patent specification[24]. The high precious metal value permits the combustion of the resin for the purpose of completely recovering the precious metals. Highly basic resins can be used for the purpose of binding cyanides, chromates, molybdates, tungstates and vanadates.

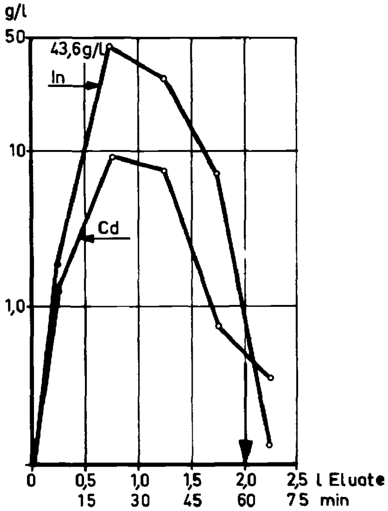


Figure 14. Separation of indium from a $CdCl_2$ solution using a complex-forming resin. 25 l passing 1 l resin in column, operation at 65°C. Cd-containing resin: In 2 mg/l. Saturated resin: In 35.8 g; Cd 6 g. Part of metal in leach: In 100%; Cd 1.2%. Elution of the resin with 2.5 l 2N-H_2SO_4. Content of 2 l eluate: In 17.9 g/l, Cd 3 g/l

Heavy metal chlorides are present as chloro complexes in solutions rich in NaCl or HCl. As their stability differs widely, selective charging with elution by steps can be utilized for the separation of, for example, Ni, Cr, Co, Fe, and Zn. *Figure 15* shows the separation: Ni and Cr are not absorbed from the 6-molar HCl solution; the resin permits these salts to pass through. Co and Fe can be eluted with 3.5- and 0.5-molar HCl, respectively. Zn salts can be eluted with water.

In principle, liquid ion exchangers can be used for ion exchange in the same way as solid resins. With regard to apparatus, the exchanger technique in extraction columns is similar to the process for removing organic impurities at liquid extraction plants. However, these are not ion exchangers.

The development of petrochemistry and the production of solvents and of organic intermediate products have made such cheap liquids available as are suited to ion exchange. For example, US research[25] shows that the selective removal of copper salts from iron-bearing mine water can be effected with the aid of the liquid ion exchangers Lix 64 and Kelex 100 (General Mills and Ashland Chemicals, USA). Residual contents below 1 mg/l of Cu can be obtained. The process, combined with percolating leaching

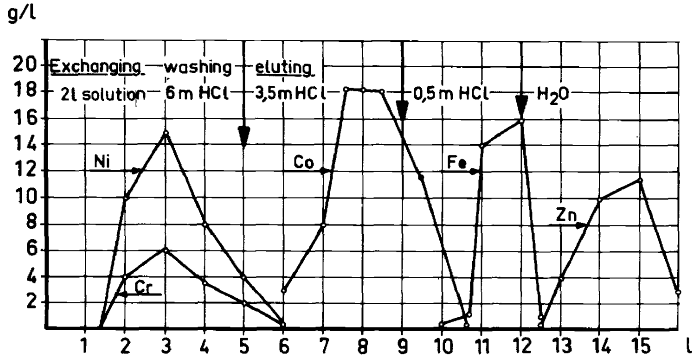


Figure 15. Separation of metals using chloro complexes in hydrochloric acid solution. Basic ion-exchange resin Lewatit M500, Separation by selective fixing and eluting of a resin column. Solution, g/l: Ni 18 : Co 22 : Cr 8 : Fe 15; Zn 13. HCl 6M

of older mine dumps, allows recovery of the copper in an economical manner. Hence, there can be no long-term pollution of underground water.

The largest solvent extraction plant to date, with a daily capacity of 190 tons of copper, is to be designed by Power-Gas. Nchanga Consolidated Copper Mines Ltd. intends to start this unique installation at Chingola (Zambia) during 1972. Waste low-grade ore will be extracted to give a copper liquor containing 1.5 g/l Cu and 4 g/l Fe. Some 130000 m^3 of liquor must be handled per day.

Without a doubt, the development of ion exchange technology will in many respects be of advantage to the treatment of waste water containing non-ferrous metals.

(10) Recovery of process water as a valuable product in the purification of waste water

It is suitable for the waste water burden of a stream from a non-ferrous metal plant to be referred to as the so-called effluent load of basic non-ferrous metals and other impurities. Generally speaking, this product of concentration and quantity is of interest to supervising authorities only with regard to the former factor. The biology of the streams and the possibility of drinking-water production directs attention to the maximum concentrations, stated in *Table 1*, of the non-ferrous metals. On the other hand, quantity is a decisive factor in the cost calculation in the basic non-ferrous metal industries[26]. Industrial purification processes should always be promoted if they cause the metal salt load to be decreased. Thus, a certain re-appraisal will be required on the side of the water experts. The British Non-Ferrous Metals Research Association dealt with the cost problem in several lectures at the 'International Conference On Air Pollution And Water Conservation In The Copper And Aluminium Industries', held in Basle, Switzerland, from October 21st to 23rd, 1969[27]. Thus, after publishing its special work on 'Effluent Treatment In The Copper And Copper Alloy Industries'[28], this organization has made another valuable contribution to water economy.

Any water recirculation economy, even if confined to some sectors of

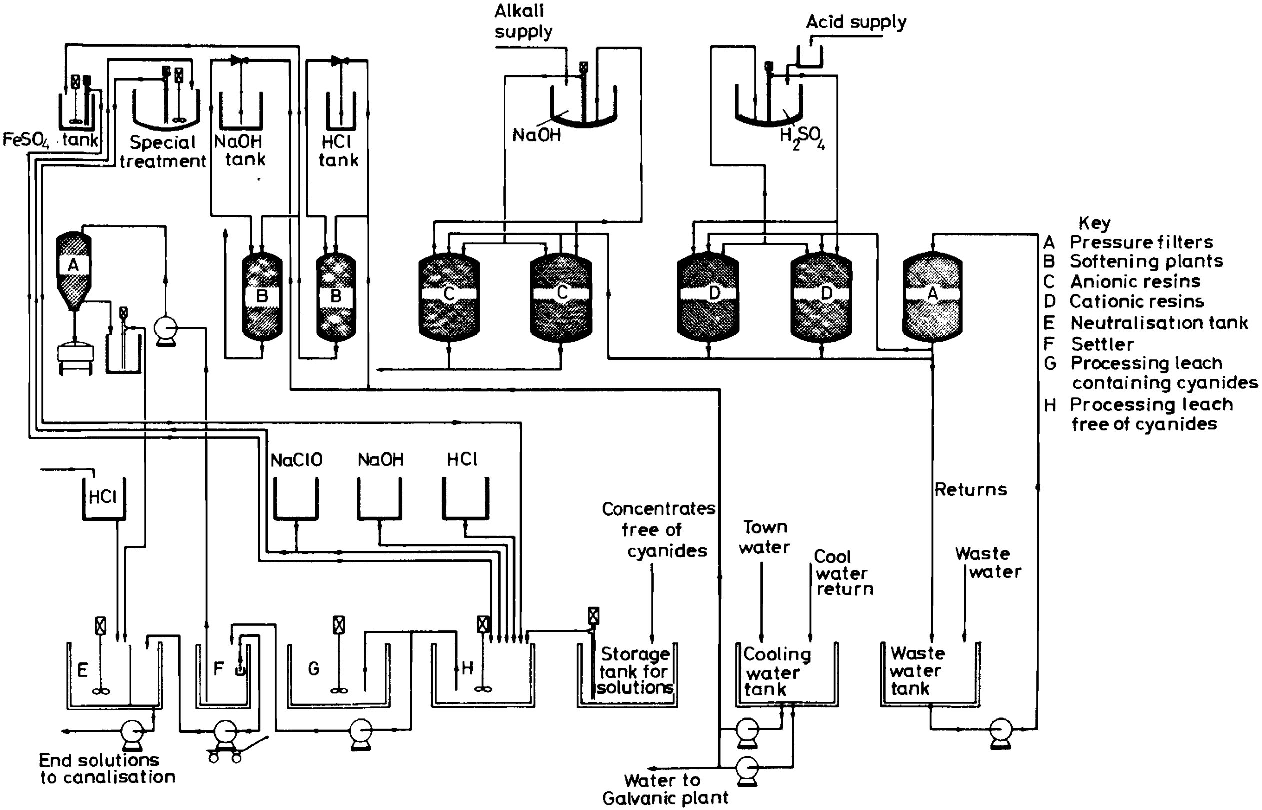


Figure 16. Flow diagram for ion-exchange treatment of galvanic effluents (Goetzelmann system)

production, would produce cost savings even if a sufficient capacity of the river allowed any amount to be withdrawn or fed in. An industrial water supply system from an adjacent river, for example, subjected to coarse purification, can be maintained at 3 to 6 atmospheres above atmospheric pressure on the basis of as low a specific power consumption as 0.15 to 0.25 kWh per cubic metre. About 0.4 to 0.7 kWh/m^3 are required for water subjected to fine purification via gravel filters. If the water can be used for a second time, or even several times, with the aids of a collecting tank, it is frequently possible for pumping costs to be lower. For example, this is the case if water of sufficient quality is required for certain equipment at higher pressures. Every non-ferrous metal plant will have to see for itself what cost savings might be achieved in its water economy.

By using the water several times, the separation of waste water of different qualities in different draining systems can often be avoided. The recovery of the non-ferrous metals at the final purifying plant will be simplified by saving water within the plant.

Of particular interest are such purifying plants as recover the raw material 'water' for the non-ferrous metal plant. Here, there are a large number of installations in the field of electrodeposition. It should, however, be taken into consideration that, mostly, drinking water is used. In some industrial areas in Europe, the price of one cubic metre of drinking water has come to be higher than the value of one kilogram of the metals zinc or lead. In such cases, the cost of an ion exchange plant for pickling and washing water is more than offset by the value of the purified water recovered.

Figure 16 gives a diagrammatic view of a large-scale plant designed for 300m^3/h (65 000 Imperial gallons/h). It is capable of stripping acidic as well as basic effluents from non-ferrous metals and cyanides. By means of very extensive recirculation and cooling, the amount of fresh water required is reduced to the amounts unavoidably lost (3–5 %). This measure has the great advantage of reducing the non-ferrous metal load in the waste water to a few per cent of the amounts resulting when fresh water is continuously supplied and used. Experience at over 400 plants in Southern Germany goes to show that, taking all cost factors into consideration, water recovery will be profitable if the price of one cubic metre of drinking water amounts to merely one sixth of the price of one kilogram of Zn.

SOME UNSOLVED PROBLEMS—TRENDS OF FUTURE DEVELOPMENTS

These examples of the special measures taken by the basic non-ferrous metal industries against water pollution show the possibilities and limits of the processes developed. Taking into consideration the widely different requirements in the different countries with regard to water economy, it is only realistic to observe that there are still a number of problems to be solved by basic non-ferrous metal industries. None of the physical, chemical, and biological purification processes are capable of extracting the metals completely. Seeing that even low concentrations of metal salts produce an unfavourable biological effect, improved technical processes must be developed.

Other fields of environmental hygiene have the particular effect of increasing the number of problems to be solved by the basic non-ferrous metal industries in connection with the prevention of water pollution. A large number of new problems are posed by the systematic deposition of slags, precipitating sludges, dusts, and other residues as well as by processes for preventing air pollution, mainly the wet processes. In the area planning sector, the locations of new basic non-ferrous metal plants will have to be selected in future with particular regard to unavoidable burdens to the waste water.

Fresh water supplies as well as sewer systems and purification plants have always been planned and built to last for decades of new developments. In most industrial countries it has become increasingly evident that water reserves are limited. Even the thermal utilization of large river systems such as that of the Rhine is limited, and this fact has to be allowed for by new large-scale power plants. For a long time, service water as a cost factor was considered unimportant to metal recovery. The water cost in the production of pig iron and steel, where the specific amount of water required is about 25 to $70 m^3/t$, is so favourable when a big stream is at hand that only the proceeds from 2 to 4 kg of steel are required to cover it. In spite of this, there is in the steel industry a process trend towards the so-called dry mill with extensive recirculation.

As compared with steel, the specific amount of water required by the basic non-ferrous metal industries is considerably higher. In addition, there is the higher expenditure of waste water treatment. Each metal plant will have to examine its own water economy conditions closely in order to meet the requirements for a higher metal yield at a cost that is reasonably economical.

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