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Recycling of Metal Containing Waste by Liquid-Liquid Extraction

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ABSTRACT

Through the years, a large number of liquid-liquid extraction processes have been proposed for metal waste recovery and recycling [1,2]. However, few of them have achieved commercial application. In fact, relatively little information is available on practical operation and economic feasibility. This presentation will give complementary information by describing and comparing three processes, based on the AmMAR hydrometallurgical concept and representing three different modes of operation.

Key Words: Liquid-Liquid Extraction/Waste Recovery/Metals/Process Operation

INTRODUCTION

In most countries, solid waste containing heavy metals such as neutralisation sludge from the plating industry and flue dust from the metal and steel industries, is currently collected and dumped in landfill, where it constitutes a perpetual toxic thread to the environment and a waste of resources. The alternatives to this landfill deposition are, either to reduce the rate of discharge at source by an individually designed recovery process or to separate and recover the metals from the collected waste at a centrally located facility. A presumption for this statement would be that companies with heavy metals in their effluents require a treatment of the total waste water streams. This could be accomplished through the relatively simple process of neutralisation, which requires only minor investment in sedimentation tanks and de-watering equipment and involves relatively modest operation costs.

Although the problem of disposal of heavy metal waste is faced by most industrialised countries, relatively few operations with respect to waste recovery have, to date, been started. Sweden still deposits its de-watered heavy metal waste in simple landfill, although Swedish industry has been in the forefront for developing both hydrometallurgical and pyrometallurgical recovery techniques. The same applies to most European countries, however, interest in environmentally safe recovery has increased in recent years and recovery plants are now being considered.

It was earlier generally believed that the at source approach with an individually designed recovery process entailed a considerable risk of investing in small, non-viable industries. Thus, it would appear that the central recovery facility was likely to be the only feasible manner in which to solve the disposal needs in a large number of point-sources. Such recovery plants, based on hydrometallurgical treatment concepts, were suggested already 30 years ago, however, at that time, these processes were doubtfully feasible. The pyrometallurgical treatment was marketed as an environmentally safe method for removing a number of different metals, among them copper, lead and zinc, from waste water sludge or mining slime and tailings. However, it was shown improbable that such processes would be economically justified in the case of relatively small volumes of waste that were likely to be at hand.

Today, to my knowledge, there is no central waste recovery plant (pyro or hydrometallurgical) in operation in Europe. However, there are many examples showing that at source hydrometallurgical recovery processes are economic in small-scale operations. To verify this observation, some process developments, based on the general hydrometallurgical concept AmMAR, will now be described in more detail.

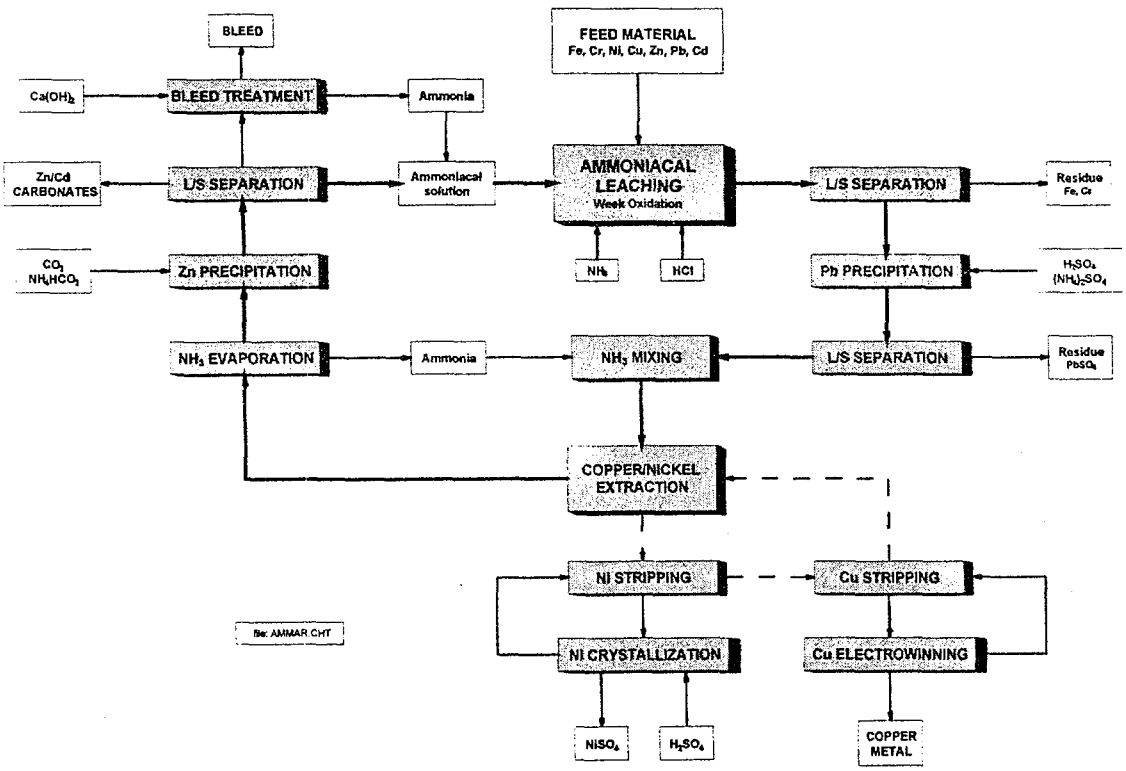
THE AmMAR CONCEPT

First, please note that the AmMAR concept [3] is not one specific process - it is a general processing route for a broad variety of feed materials. The detailed design of each specific process involves a required number of known chemical operations, combined in unique ways. The main thread is the ammoniacal solution and its extraordinary chemical flexibility.

The main metals in the feed material are iron, chromium, copper, zinc and nickel, with minor amounts of other metals e.g. lead and cadmium. Some general sources are:

- Brass mill flue dust (Cu, Zn, Ni)
- Steel mill flue dust (Fe, Zn)
- Neutralisation sludges from the plating industry (Fe, Cr, Cu, Ni, Zn)
- Accumulator scrap (Ni, Cd)

The general flow diagram below, describes the outline of the AmMAR concept for the treatment of materials containing the above mentioned metals.



- In the leaching operation, the metals copper, zinc and nickel (lead, cadmium) are dissolved as chlorides, chloro-complexes or ammonium-complexes, while iron and chromium remain in the solid residue as hydroxides.
- Lead impurities will be precipitated as lead sulphate.
- Ammonia is added in excess to form metal ammonium complexes.
- Copper and nickel are subsequently removed from the leach solution by solvent extraction. After selective stripping, nickel sulphate is produced by crystallisation and copper metal by electrowinning.
- The excess ammonia is evaporated and recovered from the remaining solvent extraction raffinate and recycled to the leaching filtrate after the lead removal.
- The remaining zinc (cadmium) is precipitated as carbonate by addition of carbon dioxide or ammonium hydrogen carbonate. After filtration the filtrate can be recycled to the leaching step.
- To maintain the water balance, especially when water containing sludge (30% DS) is treated, an effluent treatment with lime is necessary.

<u>Leaching</u>

To achieve an efficient leaching, the treatment is performed in two steps. The initial leaching step in the most complicated case, is an acid treatment containing ammonium chloride - hydrochloric acid:

$$Me(OH)_2 + 2\ NH_4Cl + 2\ HCl \rightarrow MeCl_4^{2-} + 2\ NH_4^+ + 2\ H_2O$$

$$Me(OH)_2 + 2\ HCl \rightarrow Me^{2+} + 2\ Cl^- + 2\ H_2O$$

$$MeO + 2\ HCl \rightarrow Me^{2+} + 2\ Cl^- + H_2O$$

Me stands for di-valent metals. Depending on the acidity, the chloride ion concentration and the complexing tendency of the metals, the metal oxides and hydroxides are dissolving as metal chloride salts or metal chloro-complexes or both. In general, the higher the chloride ion concentration is, the higher is the complexing tendency. The $ZnCl_4^{2-}$-complex is very strong and the formation is therefore favoured. Lead forms very weak chloro-complexes and dissolves as $PbCl_2$. The salt has a limited solubility. Elevated temperature increases the solubility and the reaction speed. In addition, pH and the ammonium chloride concentration are determined by the desired leaching action.

Trivalent metals, like iron and chromium, are dissolved by similar reactions as above. The metal chloride salts are very soluble and the most likely chloro-complexes, however not very strong, are - $FeCl_4^-$ and $CrCl_6^{3-}$. Thus, these metals are, to some extent, dissolved. Depending on the conditions, Fe(III) may precipitate again by forming the hydrous oxide goethite, FeO(OH). An oxidation of Fe(II) to Fe(III) may be necessary already in the initial stage, however, some caution is recommended as hexa-valent chromium has to be avoided. The dissolution of iron may be necessary in order to break-up iron masked metals like zinc ferrite, existing in e.g. steel flue dust.

Although the dissolution of desired metal oxides or hydroxides is good, substantial amounts of iron and chromium are present in the leach solution. This is taken care of in the second step of the leaching procedure where ammonia is added to pH > 8.5. The following reactions, exemplified by copper and iron, occur:

$$CuCl_4^{2-} + 2\ NH_4^+ + 2\ H_2O + 6\ NH_3 \rightarrow Cu(NH_3)_4^{2+} + 2\ OH^- + 4\ NH_4Cl$$

$$Fe^{3+} + 3\ Cl^- + 3\ NH_3 + 2\ H_2O \rightarrow FeO(OH) + 3\ NH_4Cl$$

Copper, zinc, cadmium and nickel ($Ni(NH_3)_6^{2+}$) form fairly strong metal-ammonium-complexes and these metals will therefore remain in solution. Cr(III), with six NH_3-ligands as nickel, and Fe(II) form weak complexes, although strong enough to interfere with the hydroxide precipitation if the excess of free ammonia is too high. In alkaline solutions Fe(II) is readily oxidised to Fe(III) by air. Ammonium complexes of Fe(III) and lead (Pb) are not known.

Of complementary interest is the possibility to dissolve metallic copper and zinc in e.g. brass mill flue dust, directly with an ammoniacal leach solution (pH about 8.5). The following expressions illustrate the reactions:

$$Cu^0 + Cu(NH_3)_4^{2+} \rightarrow 2\ Cu(NH_3)_2^+$$

$$2\ Cu(NH_3)_2^+ + 0.5\ O_2 + 4\ NH_3 + H_2O \rightarrow 2\ Cu(NH_3)_4^{2+} + 2\ OH^-$$

Finally, leaching with an ammoniacal solution containing carbonate is advantageous as such a solution has a buffering effect around pH 8,2. In fact, when a metal carbonate precipitation stage is included in the process, carbonate in the leaching stage will be difficult to avoid.

Solvent Extraction

The solvent extraction technique offers a possibility to selectively recover metals from a leach solution by the choice of operation conditions. Considerable concentration effects can be achieved by variation of the flow ratio of organic to aqueous solutions. In addition, a solvent extraction operation is flexible with respect to the composition of included components and to the size of operation, and can be made economic in small-scale operation.

Copper and nickel are transferred from the leach solution into concentrated product solutions by using a solvent extraction procedure. The ammoniacal leach solution, the aqueous feed, is mixed in the extraction mixer-settler stages, counter-currently with an organic metal extraction solution. This solution, insoluble in water, mainly consists of a metal selective, organic reagent diluted in kerosene. Nickel and copper form metal-organic compounds with the reagent, which are more soluble in the kerosene solution than in the water solution. The concentrations of nickel and copper in the ammoniacal leach solution are reduced and the resulting raffinate may therefore be almost freed from nickel and copper. In the following scrubbing stage (not marked in the figure) eliminates the carry-over of ammonia and co-extracted small amounts of zinc.

In the first section of stripping mixer-settlers, the nickel-reagent compound is split by weak sulphuric acid (controlled conditions) and nickel is transferred to an aqueous solution of concentrated nickel sulphate, from which the nickel sulphate salt can be crystallised.

In the second section of stripping mixer-settlers, the copper-reagent compound is split by concentrated sulphuric acid and the copper is now transferred to an aqueous solution of concentrated copper sulphate, from which copper metal can be produced by electrowinning.

PROCESS OPERATION MODES

Based on the AmMAR concept, three process examples will now be described. These processes represent three different modes of operation - *on-line, in-line* and *off-line.*

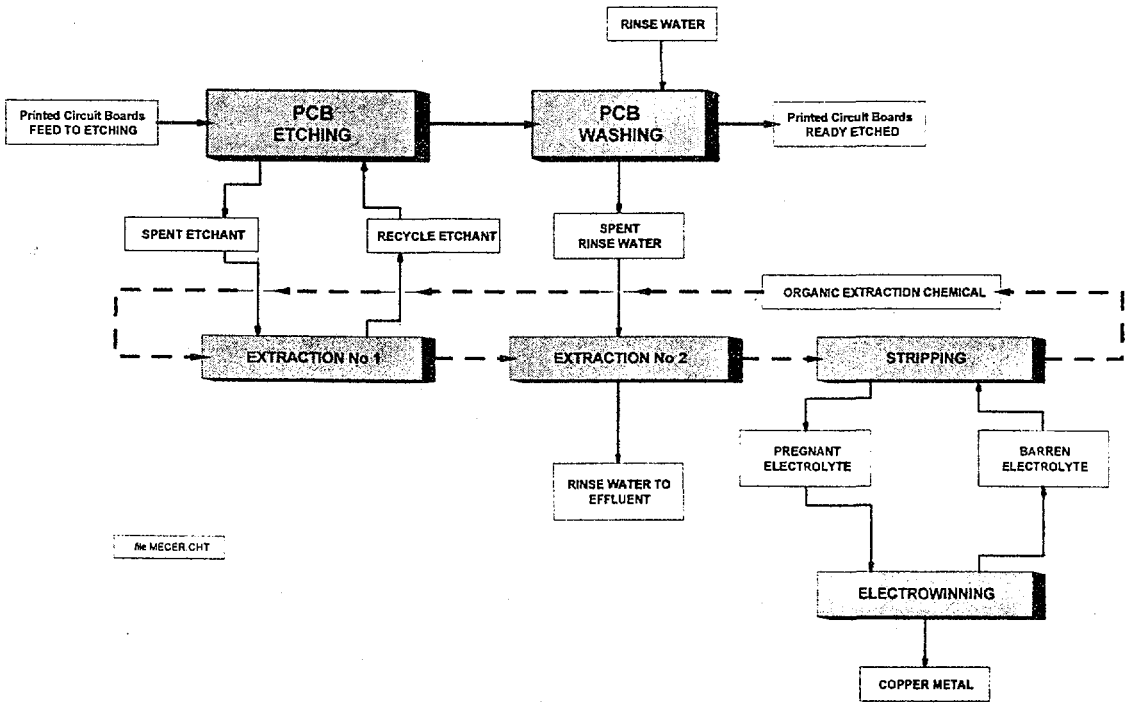
- The *on-line* process represents an operation integrated like a kidney in the main production. The solvent extraction operation gives a raffinate, which is directly returned to production to reuse the chemicals and, in addition, a product solution, which may be treated e.g. by crystallisation or electrowinning to give the product.

- The *in-line* process is a separate production unit, incorporated in the main production. Internal and external waste, such as flue dust, neutralisation sludge, slag and scrap are treated to increase the supply of feed material and to solve internal environmental problems.

- The *off-line* process is an independent production plant, treating waste materials.

PROCESS EXAMPLE 1. THE MECER PROCESS (on-line)

The etching solution used in the manufacturing of printed circuit boards in the electronics industry is very commonly an ammoniacal solution. The solution contains free ammonia, one or more ammonium salts and complex chemicals like stabilisers, catalysts etc. During etching, the copper concentration is increased. Optimal etching efficiency is obtained when the etching solution contains 140-160 g/l copper. Spent etching solution must continuously be withdrawn and replaced with fresh etching chemicals to maintain the etching efficiency constant and optimal.. It is to be noted that the spent solution is a simplified leach solution in the AmMAR concept, only containing the metal copper, and the solvent extraction procedure to follow will be the same.



In the MECER process [4], integrated (on-line) in the production, chemicals are recycled and copper recovered as electrolytic cathode copper. The process contains basically two unit operations:

- Solvent Extract (SX) for the transportation of copper out of the spent etching solution and the rinse water into the electrolyte
- Electrowinning (EW) for the production of high quality copper metal.

The solvent extraction operation contains three mixer-settler stages - one for the extraction of copper from the spent etching solution, another for the extraction of copper from the rinse water (including the cleaning of ammonia), and a third for the re-extraction (stripping) of copper to a sulphuric acid electrolyte.

In the first extraction mixer-settler, stage 1, the spent etching solution is mixed with an organic solution, containing an organic reagent, dissolved in kerosene. Part of the copper in the etching solution forms a chemical compound with the organic reagent and, as this compound is more soluble in the kerosene than in the aqueous etching solution , copper is transferred to the kerosene solution. The copper concentration, initially about 150 g/l, is in this way reduced to about 90 g/l. The treated etching solution, now capable of etching a new amount of copper, corresponding to that extracted, is returned to the etching machine.

To compensate for evaporation and drag-out losses of chemicals (about 5 %), a make-up of fresh replenisher is added to the etching machine. This make-up also contains some carbonate in order to achieve a buffering effect around pH 8.5. A pH-control unit maintains a constant pH by addition of ammonia gas.

In the second extraction mixer-settler, stage 2, the used rinse water from the etching machine is mixed with the organic solution from the first extraction. Under prevailing conditions, copper is extracted almost quantitatively, down to an amount less than 5 ppm. Part of the treated rinse water, having a pH of 9.5 and containing 0.5 g/l ammonia, is re-used as rinse water in the first rinsing stage in the etching machine.

The organic solution finally flows to the third re-extraction mixer-settler, stage 3, where it is mixed with a sulphuric acid electrolyte. The copper-organic compound is split and the copper is now transferred to the electrolyte. The organic solution, freed from copper but containing the reagent, is recycled for renewed extraction of copper in the first extraction mixer-settler, stage 1.

The copper-enriched electrolyte is fed to the electrowinning cells for precipitation of copper metal. The feed flow and current load in the cells are controlled to maintain a constant copper concentration in the electrolyte. The copper depleted electrolyte, overflowing from the cells, is taken back to the third re-extraction mixer-settler, stage 3, for renewed enrichment of copper.

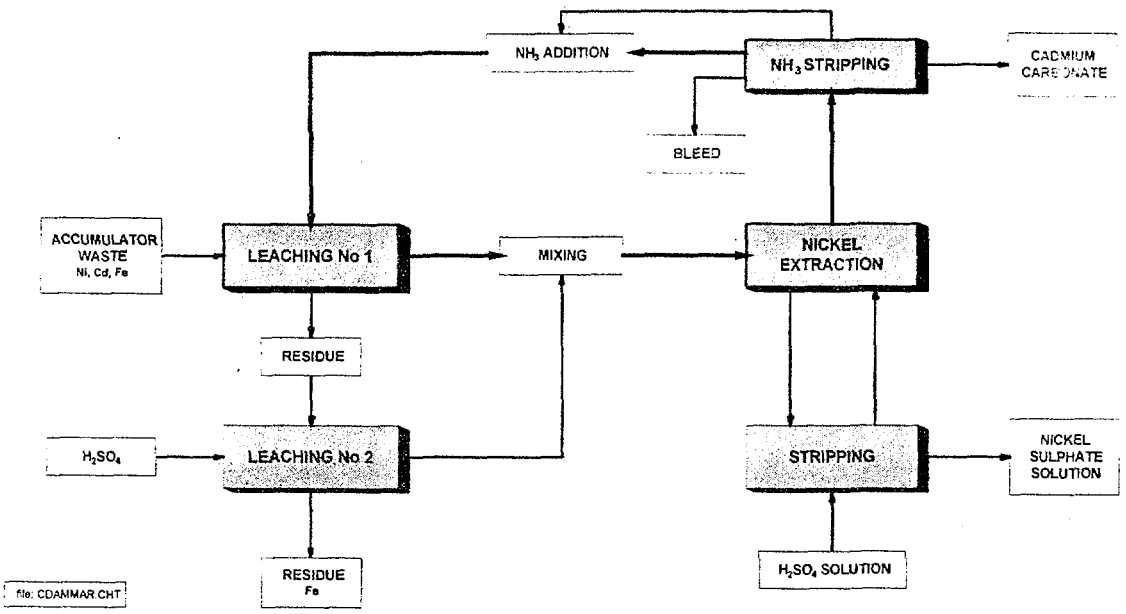
PROCESS EXAMPLE 2. THE NIFE/CD PROCESS (in-line)

The main leaching procedure to dissolve the valuable metals nickel and cadmium from worn-out accumulators is performed with an ammonium carbonate solution. This procedure has several advantages; iron will remain in the leach residue, nickel and cadmium are relatively easily leached and form metal-amine complexes in solution and, finally, the buffer capacity of the solution facilitates solvent extraction of metals with hydrogen ion exchange reagents.

Due to chemical passivation in "old" waste materials, a subsequent leaching of the leach residue with sulphuric acid is necessary to achieve yields much greater than 95 %. If pH in this second treat-

ment is kept about 3, leaching of iron is negligible. Also, to reduce iron in the leach solution, spent potassium hydroxide electrolyte from discarded batteries, can be used for iron hydroxide precipitation.

Nickel is extracted from the leach solution using an α-hydroxyoxime. Significant amounts of ammonia and cadmium are co-extracted. Scrubbing is therefore performed, first with an ammoniacal carbonate solution and then with very diluted sulphuric acid. Nickel is stripped with sulphuric acid to produce a nickel sulphate solution, containing 90-100 g/l nickel. This solution is used directly in the production of new accumulators.



The presence of carbonate in the ammoniacal system offers a possibility of controlling the conditions for the formation of cadmium carbonate. Thus, after separation of nickel in the solvent extraction loop, cadmium is precipitated as carbonate. The ammonia concentration is reduced by thermal stripping. Some carbon dioxide will also be stripped. The precipitation is made complete by cooling the solution and by addition of a carbon dioxide purge. After filtration of cadmium carbonate, the filtrate is used for absorption of the stripped ammonia and the resulting solution is recycled to leaching. The cadmium carbonate precipitate is directly used in the main production.

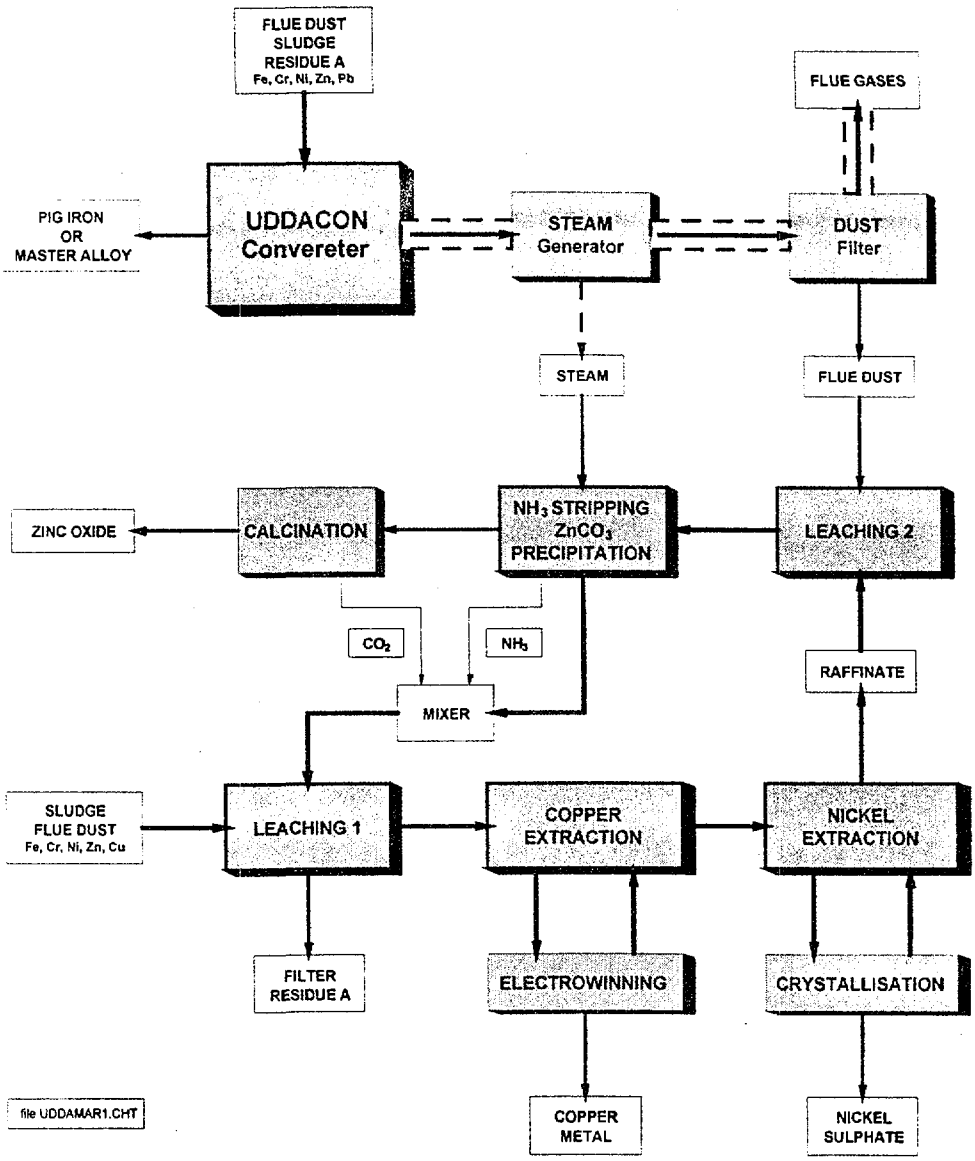
It is necessary to bleed about 25 % of the filtrate from the carbonate precipitation to keep the material balances. This large bleed is due to the sulphate added in the sulphuric acid leach and to the fact that the waste material contains considerable amounts of alkali (KOH) and water. The bleed needs special treatment to recover ammonia and to produce an environmentally acceptable effluent.

PROCESS EXAMPLE 3. THE UDDAMAR PROCESS (off-line)

The UDDAMAR process (5) is a pyro/hydro metallurgical process concept to be used in a centrally located recovery plant for the treatment of oxidic and hydroxidic waste materials from steel and metal works, including the plating industry. The process, shown in the figure below, is based on the use of a pyrometallurgical treatment in the Uddacon induction converter, combined with the AmMAR hydrometallurgical treatment for copper, nickel and zinc.

Pyrometallurgical Treatment

The supply of pulverous feed material to the furnace in the pyrometallurgical part of the operation is performed through an injection tuyere, situated below the metal surface. The material is blown into the melt, suspended in a small quantity of gas. All reducible metals are reduced in the Uddacon furnace as it is very efficient for reducing purposes. The non-volatile metals are trapped and alloyed in the melt. The volatile metals pass the converter as metallic vapours. Non-reducible oxides are collected in the slag.



For the treatment of ferruginous powders in the Uddacon converter, dry dust is mixed with coal powder as reducing agent and, if necessary, also with fluxes. The mixture is blown into the furnace in

which pig iron is used as starting melt. Iron, nickel and other metals with low vapour pressure are reduced and collected in the melt. Zinc and other volatile metals are reduced to metallic vapours and will escape through the mouth of the converter, outside which they are combusted by excess air and will form fumes of corresponding oxides. The secondary dust is recovered by filtration and leached in the hydrometallurgical part (Leaching 2).

The thermal energy, generated in the flue gases from the furnace, is used for drying the feed material and for stripping ammonia.

Hydrometallurgical Treatment

The first step of the hydrometallurgical part of the operation, the feed material is leached with a ammoniacal solution. Metals like copper, nickel and zinc form metal-amine complexes and will therefore dissolve in the leach solution. Other metals like iron and chromium form not soluble hydroxides and will remain in the leach residue. This residue is dried and mixed with the feed to the Uddacon converter.

Copper and nickel are separated from the leach solution by solvent extraction, either by differential extraction of the metals, one by one, or by co-extraction, followed by selective stripping. Zinc extraction can be neglected. Products are copper cathodes and nickel sulphate.

To treat the secondary dust from the Uddacon converter and, in the same time, increase the zinc concentration in the solution, the dust is leached with the ammoniacal raffinate from the Cu/Ni extraction. Zinc carbonate is then precipitated by thermal stripping of ammonia, cooling and addition of a carbon dioxide purge. The zinc carbonate is calcined to zinc oxide and liberated ammonia and carbon dioxide are recycled to the leach solution.

GENERAL COMMENTS ON THE THREE PROCESSES DESCRIBED

Process Development

The initiative to develop an *on-line* or an *in-line* process very often comes from an industry and emanates from internal environmental problems. The development of the process may be sponsored by the industry, the government or by private R&D organisations, which may be attracted by the general market potential. The incentive of installing such a process in the industry is, besides the environmental advantages, the possibility of recycling expensive chemicals and of optimising the main production.

The incitement to build an *off-line* process is often the result of an environmental problem, which is tending to disturb the public at large. The initial money comes from governmental funds, although industry may actively participate. As industry usually has limited knowledge of such general recovery projects, the development work is predominantly performed by R&D institutions or organisations. Close co-operation with the industry concerned is generally the case.

The development conditions feasible for an *on-line* or *in-line* process are somewhat different from those of the *off-line* process, regarding the freedom in feed materials and end products. This is especially characteristic for the *on-line* process, where the feed solution is dependent on optimal working conditions in the main process and therefore is quite fixed in composition. In addition, the

product solution must have an accurate specification in order not to disturb the main production. In the development work, a good knowledge of the main operation is necessary.

Process Specification and Operating Conditions

The strong link between the *on-line* process and the main operation is the cause of a large degree of automatisation. Absence of easily adjustable valves and an on/off mode of operation are recommended. The fact that the industry in question has neither competent knowledge nor specially experienced personnel, means that services and troubleshooting have to be arranged by an external organisation. A certain independence in utility time of the auxiliary and main processes is arranged by built-in buffer capacities.

The *in-line* processes have to be rather flexible with respect to the physical conditions and to the composition of the feed material. This is very important, as this may be the decisive incentive for the investment. In both *in-line* and *off-line* processes, treatment of bleed streams is necessary and is often extensive.

Process Economy

Some summarised data on the three processes are given below:

		MECER	NIFE/CD	UDDAMAR
Annual feed material		600 m^3	2,400 tons	25,000 tons (7,500 ton DS)
Products				
Copper metal, USD 2.25/kg		30 tons	-	300 tons
Zinc oxide, USD 1.60/kg		-	-	1200 tons
Nickel sulphate, USD 2.90/kg		-	1,300 tons	2000 tons
Cadmium carbonate, USD 3.20/kg		-	300 tons	-
Pig iron, USD 0.12/kg		-	-	1650 tons
Master alloy (Cr part), USD 1.20/kg		-	-	750 tons
Saving in etchant, USD 0.85/lit		200 m^3	-	-
Direct investment	kUSD	**300**	**5,200**	**15,000**
Operation cost	kUSD	**45**	**700**	**4,000**
Product value	kUSD	**240**	**4,750**	**7,500**

In general, the direct investment is highest for the *off-line*, and lowest for the *on-line* processes, as they can be built in very small units. The decision time for the investment usually drastically increases in the order *on-line* < *in-line* < *off-line*. The big investment, the relatively low return, the unstable value and uncertain situation of feed materials (raw material or waste) and finally, the fluctuating prices of end products characterise an *off-line* metal waste recovery process. These facts indicate the necessity of financial support from the government to secure the realisation of such a project.

The operation costs are comparably lower in *on-line* and *in-line* processes because of the integration in the main operation. The *off-line* process has for example administration costs, which can be almost neglected in *on-line* and *in-line* processes. The same for work supervision, especially at night, which can be shared with the main operation. *On-line* solvent extraction processes have very low costs for chemicals and energy. The consumption costs for an *in-line* process is dependent on the bleed stream treatment and on the possibility of using intermediate products in the main operation. In an *off-line* process, all products have to be of commercial specifications.

The economic result (feasibility) of an *off-line* solvent extraction process is comparable with all other hydrometallurgical operations and is highly dependent on price and quality of the metals produced. Adequate quality and quantity of cheap feed materials are also essential. It is very important to consider the fact that the transformation of waste to raw material usually involves a drastic increase in the value of the feed material. For *on-line* and *in-line* processes the economic result can't be isolated to the auxiliary process, but is the result of the combined effects on the total operation.

Conclusions

Considering the general conditions for an *off-line* (and many times also for an *in-line)* metal waste recovery plant, a conclusion may be reached - it would be desirable to store all metal waste under controlled conditions and with no mixing or dilution. Future development will definitely result in new and more economic recovery procedures. As metal-containing wastes differ widely in nature and complexity selective separation techniques such as solvent extraction will be of increasing importance.

The three process examples given, are all tested in pilot plant scale, in their entirety or in independent parts. Experience shows that metal waste recovery, integrated or incorporated in the main production is the most attractive process alternative. Over 100 MECER (*on-line)* processes are in operation world wide. Only one NIFE/CD (*in-line*) process has been built. However, similar processes for copper and zinc are in operation. No decision to build a full scale UDDAMAR process has been taken, mainly due to the very uncertain availability and cost of feed materials.

The reasons for the success of the MECER (*on-line*) process are the moderate investment and the fairly rapid return of assets, which lead to rapid decisions. Internal recycling, new possibilities of cheap feed material sources and an internal solution of the environmental problems are other strong incentives for this type of process.

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