

The MAR Concept

General Description

The MAR Project (Metals and Acids Recovery) was aimed to evaluate hydrometallurgical process technology for the recovery of copper, zinc and nickel from waste materials. Two main process routes have been developed:

- H-MAR based on sulphuric acid leaching
- AmMAR based ammoniacal leaching

Both these process routes can be adopted for metal containing waste materials. The optimal choice, however, mainly depends on the origin of the material, on which metals shall be recovered, on what products shall be produced and of cause, on the process economy.

References.

MAR-Hydrometallurgical Recovery Processes, Proc -Int Solv Extr Conf, Toronto 1977

Some Hydrometallurgical Processes for the Reclamation of Metal Values. Proc Int Waste Treatment and Utilisation Conf, Waterloo, Canada 1978.

The H-MAR Processing Route



Block diagram:

Extraction of Copper and Zinc from Weak Acid (H₂SO₄) Effluents

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The H-MAR process can be regarded as two separate, interconnected processes, one for copper recovery and one for zinc recovery.

In the copper circuit, copper-rich material is leached in a pH controlled leach at 60 °C to the final pH of 2 - 2.5. Oxidizing conditions are maintained, e.g. by addition of MnO₂, to promote copper dissolution and to prevent cementation of metallic copper when the feed material contains metallic zinc (brass or iron). The leach solution is filtered and fed to a solvent extraction circuit in which copper is extracted in four stages with a kerosene solution containing a copper selective reagent. The stripping is performed in three stages with sulphuric acid electrolyte. Copper metal is recovered from the electrolyte by electrowinning.

The zinc circuit consists of a similar pH controlled leach at 60°C and under oxidizing conditions. Zinc flue dust with low copper content is leached with the copper barren raffinate and with part of the zinc raffinate. The pH in the zinc leaching operation is maintained at about 2 for most of the leaching time and then slowly raised to a final pH of 4.5, bringing down the iron level to below 10 ppm. The leach solution is filtered and cleaned from impurity metals such as Cu, Ni and Cd by an ordinary cementation procedure, again filtered and finally fed to a solvent extraction circuit. Zinc is extracted in three stages with a kerosene solution containing a zinc selective reagent. The amount of zinc transferred in the extraction procedure can be maintained as high as 20-25 g/l, because the remaining zinc in the raffinate is recycled to leaching. Stripping of zinc is performed in two stages with sulphuric acid electrolyte and zinc metal is recovered from the electrolyte by electrowinning.

The H-MAR process flow sheet was first tested for direct leaching of steel mill flue dust and production of zinc metal by electrowinning. The tests were performed in a continuously operating pilot plant, producing 10-20 kg/day zinc metal. The same pilot plant was then used for treating copper/zinc-rich brass mill flue dust in a closed loop operation, recycling all the zinc solvent extraction raffinate to the copper circuit leach section. In the zinc circuit leach section, only the amount of zinc rich dust necessary for neutralization of the copper solvent extraction raffinate was used. The results obtained from the pilot plant tests were used for estimating the economic data for both alternatives.



Leaching

Solvent Extraction

Electrowinning

The AmMAR Processing Route



The AmMAR concept 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 ammoniaammonium chloride or carbonate leach solution and its extraordinary chemical flexibility.

The general outline of an AmMAR process for treatment of a material, containing two or more of the metals iron, chromium, copper, nickel and zinc, includes the following process steps:

- The primary separation occurs in the leaching procedure, where the metals copper, zinc and nickel are dissolved as metal ammonium complexes, chlorides or chloro-complexes, while iron and chromium remain in the solid residue as hydroxides.
- Copper and nickel are subsequently removed from the leach liquor by solvent extraction. After selective stripping, nickel sulphate is produced by

crystallization and copper metal by electrowinning

- The excess ammonia is evaporated from the resulting extraction raffinate and absorbed in the leaching filtrate.
- The remaining zinc in the extraction raffinate is precipitated as carbonate by the ammonium carbonate already in the solution or by addition of carbon dioxide. The resulting filtrate is recycled to the leaching step.
- To maintain the water balance, especially when water containing sludge is treated, an additional effluent treatment with lime, followed with ammonia evaporation, is necessary

The two unique operations in this process is the leaching and the solvent extraction with selective stripping of copper and nickel.