

## Leaching behavior of several zinc rich residues in a hydrometallurgical recycling process

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### Abstract

The leaching of metals contained in spent Zn-MnO<sub>2</sub> batteries and electric arc furnace (EAF) dusts using sulfuric acid solutions was studied, in order to evaluate the feasibility of simultaneous treatment of both wastes by a hydrometallurgical process.

In both residues, a substantial quantity of zinc was solubilized (about 100% in batteries and 70-80% in EAF dusts) in diluted acid solutions and room temperature, corresponding to the reaction of zinc oxide species. Other species were more refractory to the chemical attack, namely the manganese (III or IV) oxides in batteries and the zinc ferrite in dusts, requiring higher temperatures (e.g. 90°C) and higher leachant concentrations. Lead present in EAF dusts was not solubilized in sulfate media, thus remaining in the leach residue. Results seem to confirm the possibility of treatment of both zinc-containing residues by the same hydrometallurgical process, eventually involving two leaching stages – diluted acid leaching and hot acid leaching – followed by solution purification through iron precipitation and Zn/Mn separation and recovery. Concerning lead, a second leaching circuit in chloride media could be developed for its potential recovery.

### Introduction

The implementation of recycling processes usually faces difficulties related with economical issues. Normally the adequate production capacity for a process to be economic is larger than the available residues. A possible solution to overcome this problem is to treat several residues, coming from different sources but having similar chemical characteristics, in the same plant. Such hypothesis requires a precise evaluation of chemical behavior of each residue component.

Zinc is a metal present in several wastes. Besides others, spent Zn-MnO<sub>2</sub> batteries and EAF dusts are considered important residues due to their potential environmental impact. Both residues have zinc and iron as major components, being also present large quantities of manganese (in batteries) and lead (in dusts). In both wastes, zinc is essentially in zinc oxide form but secondary Zn species can also be found such as combined species like Zn-Mn and Zn-Fe oxides. The evaluation of the leaching behavior of these species is crucial for the development of a hydrometallurgical process to be applied to mixtures of such residues. In this paper, the results of leaching tests with sulfuric acid solutions of the two above mentioned residues are presented and discussed.

### Results and Discussion

The leaching tests were carried out in orbitally shaken glass vessels under temperature control. EAF dusts were provided by a Portuguese steel production company and were washed with water and dried before used. Batteries were collected in a domestic collection point and the cells of the Zn-MnO<sub>2</sub> system were sorted manually. The resulting sample contained about 89 w% of alkaline and 11 w% of saline batteries. The sample was shredded in a cutting mill with a 6 mm discharge grid resulting a grinded material with 1.2 mm average particle size. Chemical characterization of both wastes is presented in Table 1.

The leaching tests of both residues was carried out for 4 hours at liquid/solid ratio of L/S=20 L/kg and at two temperatures – 25°C and 90°C. Several H<sub>2</sub>SO<sub>4</sub> concentrations were experimented, aiming at to evaluate the reactivity of the several species. The results presented in Fig. 1a show the behavior of metal species in EAF

dusts, being very dependent from temperature and acid concentration. Zinc dissolution up to 80% occurred at relatively low concentrations and stabilized at about 0.3M  $H_2SO_4$ , corresponding to the reaction of ZnO. At room temperature the remaining zinc ( $ZnO \cdot Fe_2O_3$ ) did not react even using higher acid concentrations. In fact, the Fe reacted in the same conditions was only 15% probably due to an easily soluble iron oxide. At 90°C the zinc dissolved up to 100% and was accompanied by the dissolution of Fe up to 80%. Part of the iron (about 20%) remained insoluble, probably referring to more refractory Fe oxides like  $FeO \cdot Fe_2O_3$ . Lead dissolution was negligible due to the low solubility of lead sulfate, allowing further selective recovery in a chloride leaching step.

Table 1 – Chemical composition (main elements) of EAF dusts and spent Zn-MnO<sub>2</sub> batteries.

|                               | Elemental composition (%) |    |     |     |     | Main Species  |
|-------------------------------|---------------------------|----|-----|-----|-----|---|
|                               | Zn                        | Fe | Mn  | Pb  | Ca  |   |
| EAF dusts                     | 33                        | 20 | 1.5 | 4.5 | 3.9 | ZnO, ZnO·Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>                                  |
| Zn-MnO <sub>2</sub> batteries | 19                        | 24 | 25  | -   | -   | ZnO, ZnO·Mn <sub>2</sub> O <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub> , MnO <sub>2</sub> , steel scrap |

Concerning batteries leaching, the results achieved are presented in Fig. 1b. It is also shown that metals dissolution was quite dependent from acid concentration and in less extent from temperature. Zinc oxide reacted easily being overall Zn dissolution achieved at 0.35 M  $H_2SO_4$ . Manganese leaching was more dependent from the acid concentration requiring values higher than 0.50 M to allow obtaining recoveries near 80-90%. In these conditions, the iron present in scrap reacted until 50-60% dissolution, being therefore an important contaminant of the final liquors.

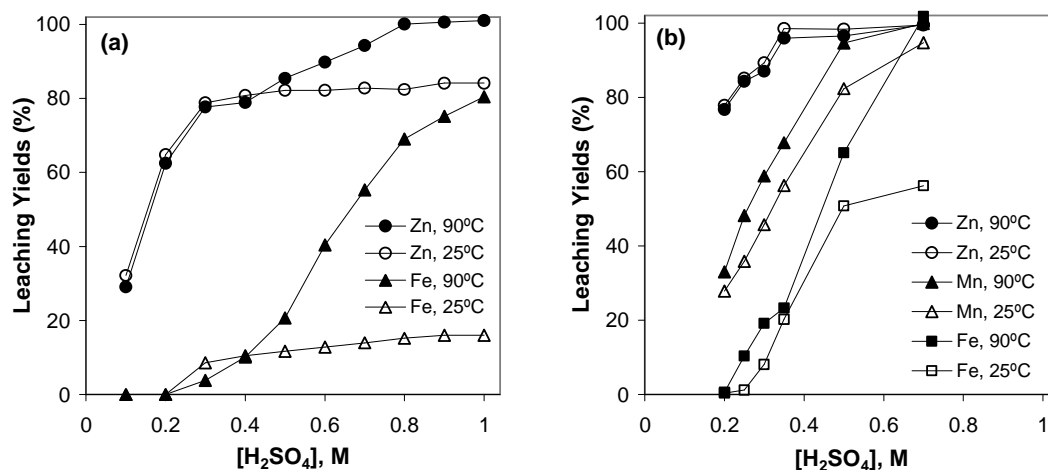


Fig. 1 – Leaching yields of metals contained in (a) EAF dusts, and (b) spent Zn-MnO<sub>2</sub> batteries, for different acid concentrations and two reaction temperatures (L/S = 20 L/kg, time = 4 h).

The results obtained demonstrated that the treatment of EAF dusts and spent batteries can be performed by the same process. In both residues, the ZnO species is very reactive in acid media while Zn-Mn or Zn-Fe oxides are less soluble requiring more aggressive leaching conditions. These differences in reactivity of the several species indicate the possibility of using a two-stage countercurrent leaching process. This approach can permit reagent (acid) and energy savings. In the first stage, the residues contact with a relatively diluted acid solution coming from the second stage (e.g. 0.3-0.4 M) at room temperature, where most of the zinc is dissolved. The remaining solids are therefore introduced in second reactor, at higher temperature (about 90°C) where the remaining zinc (present in mixed oxides) and manganese are leached with a fresh sulfuric acid leachant. Besides energy and materials optimization, this arrangement minimizes iron contamination, decreasing costs in further purification operations.

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