

PHYSICAL PROCESSING EFFICIENCY OF SALINE vs. ALKALINE SPENT BATTERIES

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Abstract

Physical processing of spent batteries which includes shredding and sieving operation is the first step for chemical treatment by hydrometallurgy. A laboratory study was carried out to evaluate physical processing efficiency, by analysing the resulting particle size, of alkaline and saline mignon-type Zn-MnO₂ batteries. After shredding with a tip shredder, results obtained showed that alkaline batteries were more efficiently size reduced than saline batteries. Difference in particle size distribution was larger for granulometric fraction -20+11.2 mm and also higher for saline batteries. Average diameters (d_{50}) for saline and alkaline batteries were respectively 9.1 and 6.2 mm. Chemical composition carried out on several granulometric fractions allowed to identify metals distribution through size categories. This analysis showed that zinc concentration with the grain size was almost constant, while manganese decreased when particle size increased. More than 95% of iron scarp from the battery cases had a particle size higher than 5.6 mm.

Introduction

Recycling process of spent batteries includes physical unit operations which involves a fragmentation step in order to open the battery cases and to allow the access of chemical reactants to the electrode materials, on further chemical unit operations. Shredders are usually used for that purpose, using cutting mechanisms and allowing efficient fracture of residues in order to promote further processing of the contained materials. Batteries are complex products with a large variety of sizes and shapes which causes serious difficulties for predicting and carrying out its fragmentation.

Domestic-type batteries are essentially of the Zn-Mn systems and with cylindrical shape, varying from the large size Mono (or D) type to the small size Micro (or AAA) type [1]. Recycling of batteries involves collection, sorting [2] and metallurgical processing [3, 4]. In some processes, the first step of metallurgical processing is dismantling and size reduction by shredding. Research work on spent batteries considering grinding/shredding and physical separation of fractions is scarce [5-7], but investigation in this domain is very necessary.

The different characteristics of batteries found in household applications, like size, shape and electrochemical system, can influence the shredding and subsequent physical and chemical processing. In Zn-Mn based systems, saline (Zn-carbon) and alkaline batteries are the main representatives, and both constitute usually more than 80-90% of domestic-type flows. These two types of batteries have different assemblage and that is a factor with possible effect on the

mechanisms of fracture and grinding, affecting consequently the fragmentation yields. In this work, the effect of type of battery in the shredding efficiency is studied using a laboratory shredder, through the evaluation of the particle size and elemental chemical distribution of Mignon-type spent saline and alkaline batteries.

Experimental

Batteries used in this work were spent alkaline and saline cells of the Mignon (AA) type, collected from a household disposal point. Samples of each type of batteries were manually separated from the bulk and then shredded with a laboratorial tip shredder (Erdwisch mod. EWZ 200), using a bottom sieve of 6 mm. The shredded materials were wet sieved by a series of sieves and an electromagnetic vibrator equipment (Retsch AS-200). The fractions obtained were dried and weighted, in order to evaluate the resulting size distribution. Chemical composition of the shredded materials was accomplished by Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF, Spectrace QuanX) and validated by Atomic Absorption Spectrometry (AAS, GBC 906AA). Analysis by AAS was carried out after solubilizing solid samples by acid digestion in microwave furnace (CEM MDS-2000).

Results and Discussion

Battery components and shredded materials

Alkaline and saline batteries have essentially the same chemical principles differing in the electrolyte media (potash and chloride salts, respectively). However different reaction products are expected due to the presence of different media. Concerning the battery assembling there are some substantial differences as can be seen in Fig. 1. In alkaline batteries the zinc anode is present as a paste in the interior while in saline batteries it appears as an exterior ring. The cathode containing the manganese compounds and the graphite powder is in the opposite places (in the exterior in alkaline batteries and in the interior in saline batteries). The shredding of the batteries was efficiently accomplished with the laboratorial tip shredder resulting heterogeneous grinded fractions (Fig. 2). Large fragments were basically steel scraps with some aggregated electrode particles while in the fines the electrodes are mostly predominant. Note that only about 50% of the material passed through the bottom sieve, thus a substantial part remained inside the shredder, but even that portion was sufficiently grinded to attain liberation of electrode particles and to allow accessibility of reagents in further chemical processing steps.

Particle size analysis of shredded batteries.

Particle size analysis by wet sieving on both shredded batteries was carried out to evaluate the resulting fractions. Granulometric curves were therefore calculated (Figure 3) where it can be observed that size reduction is more efficient in alkaline batteries. The main difference in size distribution is in the major size class (-20+11.2 mm, average 15.6 mm) where saline batteries have almost 35% of their weight while for alkaline batteries the corresponding values are only 14%. This behavior is due to the more brittle feature of alkaline battery cases. Characteristic diameters found for alkaline and saline batteries where, respectively: $d_{10} = 0.14$ and 0.56 mm; $d_{50} = 6.2$ and 9.1 mm; $d_{90} = 11.8$ and 14.7 mm. Besides the relatively high dimension of the resulting fragments, the shredding was considered successful in both batteries since allowed the opening and grinding of exterior cases and subsequently the inside electrode powders became liberated or at least accessible.

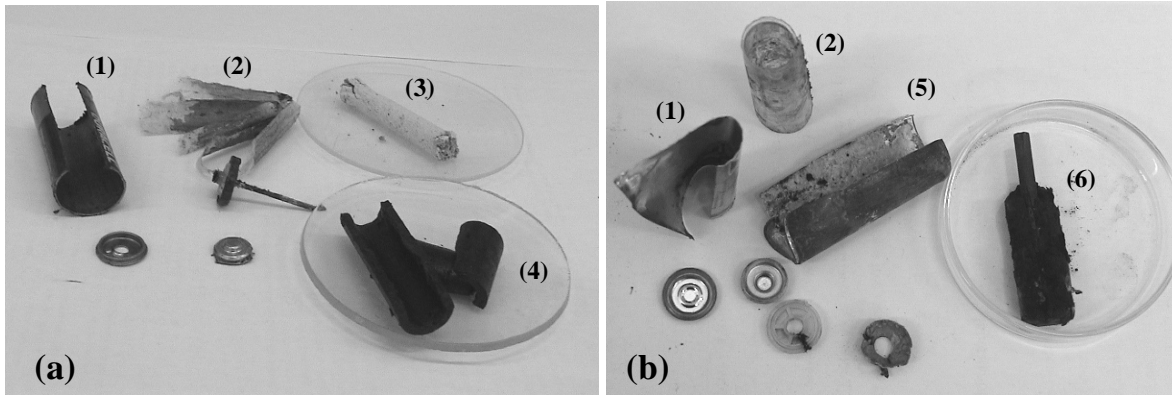


Figure 1. Dismantled (a) alkaline and (b) saline Mignon-type batteries. (1) steel cases; (2) plastic separators; (3) zinc paste anode; (4) manganese cathode; (5) zinc sheet anode; (6) manganese cathode.

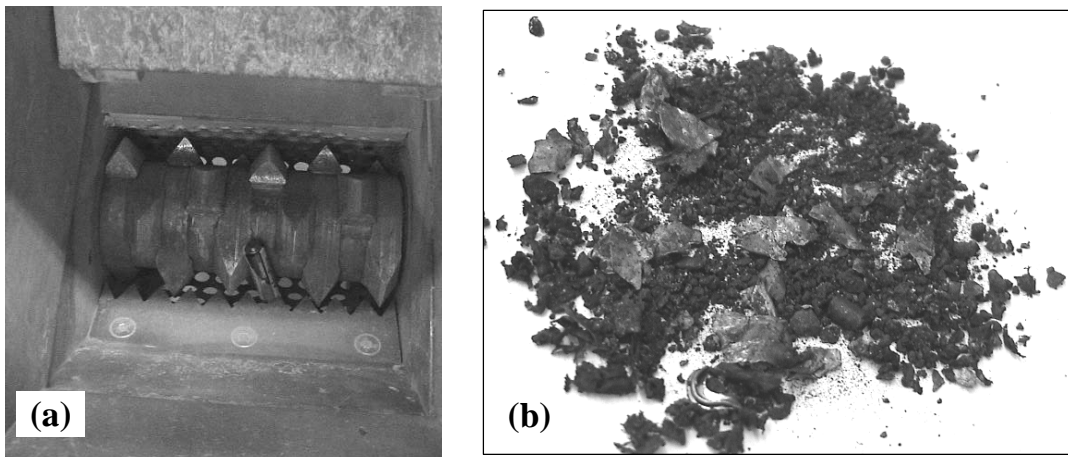


Figure 2. (a) Shredder detail (single-shaft tip cutters) and (b) resulting shredded material.

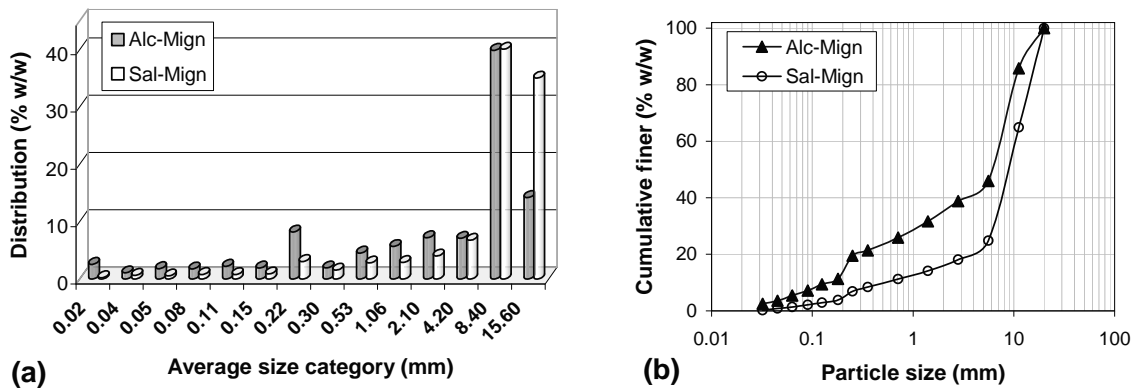


Figure 3. Granulometric curves of shredded alkaline and saline batteries: (a) Size distribution by granulometric classes (values of x-axis are the average of size range in each class); (b) cumulative finer curves.

Chemical characterization of shredded fractions

Elemental chemical analysis of battery shredded fractions was accomplished in order to assess the metal distribution with particle size. The three main metals contained in batteries – Zn, Mn and Fe – were therefore followed in the several grinded samples (Figure 4). Differences in metal distribution for the two types of batteries were not significant. Zinc distribution is almost constant in fine fractions and decreases slowly in large fractions. This means there is a substantial anodic material aggregated with the coarse steel scrap. Concerning manganese, the distribution is more variable, decreasing strongly in the gross fractions. The iron contained in the steel cases is almost totally present in the larger size fractions. In the fines (size less than 0.36 mm), iron concentration in alkaline and saline battery samples was below 0.2% and 1.0%, respectively. The chemical analysis also shows that batteries are highly concentrated metal bearing materials with potential value. Average battery compositions for the three main metals are 18-20% Zn, 18-23% Mn and 23-26% Fe.

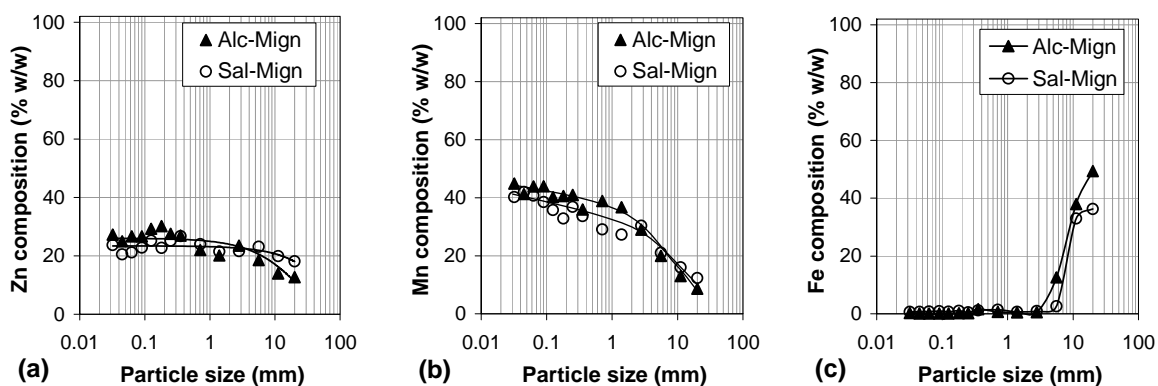


Figure 4. Distribution of (a) zinc, (b) manganese and (c) iron with particle size of shredded batteries.

Evaluation of metal recovery yields in physical separation by sieving

In the hydrometallurgical processing iron usually constitutes a problem since causes strong interferences in the separation and recovery operations of the other metals. Therefore its removal from the chemical processing circuits is greatly advisable. In this study, it was found that iron is mostly present in coarse fractions and consequently its removal by sieving is an alternative to assess. Combining chemical composition with weight distribution along the particle size, it was possible to determine the metal recoveries in the form of cumulative curves (Figure 5) which represent the percentage of each metal recovered or lost after sieving at a preset size. The difference between the recoveries of two metals represents a selectivity indicator which is plotted in Figure 6. Maximum selectivity between Zn and Mn over Fe was found at 5.6 mm particle size, which means that sieving at this aperture the separation of zinc and manganese from iron is maximized.

For alkaline batteries, about 96% of iron is removed above 5.6 mm, while about 40% and 28% of zinc and manganese are lost in this fraction (see recovery curves, Figure 5). As a result the recovery yields of zinc and manganese in the infra fraction are respectively 60% and 72%. In the case of saline type batteries, the iron removal above 5.6 mm attains almost 99% whereas zinc

and manganese lost are estimated as 71% and 59%, being the recoveries in the fines 29% and 41% respectively.

Removal of iron by sieving involves substantial lost of zinc and manganese since part of the wet powders containing the electrodes are stuck in the steel scrap and are not easily removed by physical methods. This behavior is principally encountered in the processing of saline batteries where losses are really important. It seems that other operations could be included to avoid it, such as a washing step in strong stirring conditions or other disaggregation method. This can be tested in further work.

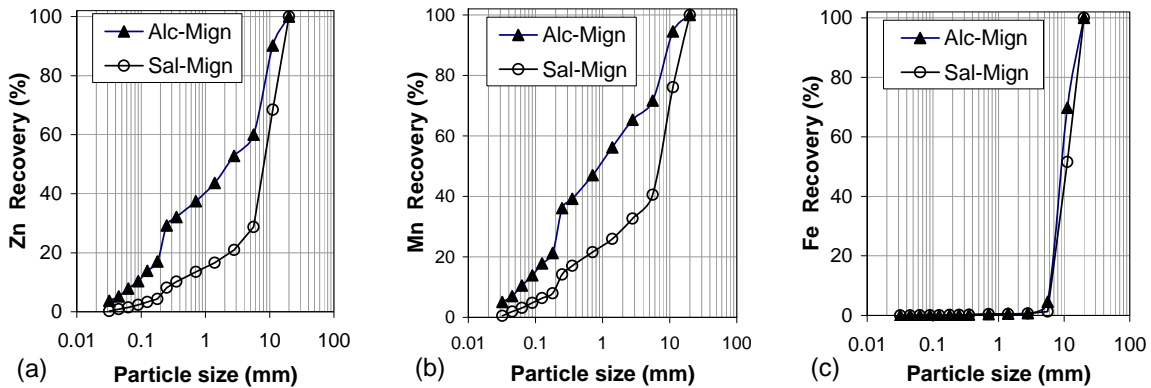


Figure 5. Cumulative recovery curves of (a) zinc, (b) manganese and (c) iron with particle size of shredded batteries.

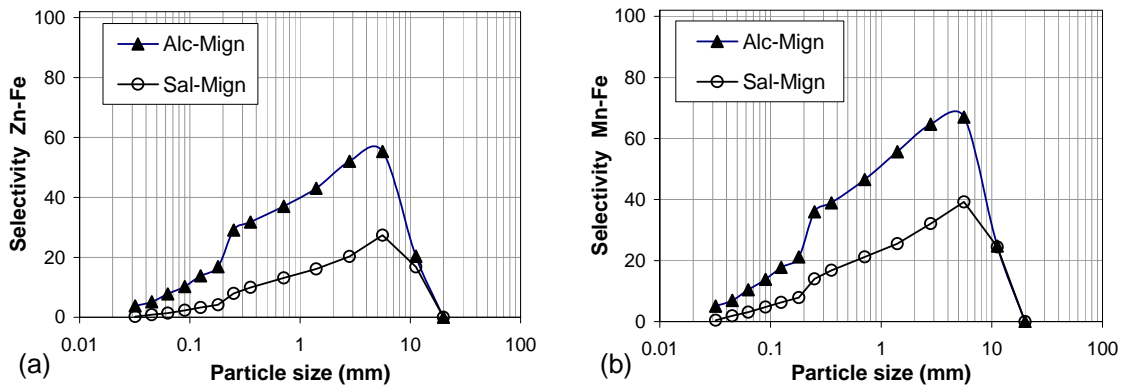


Figure 6. Selectivity of (a) zinc and (b) manganese vs. iron with particle size, based on the recovery differences.

Conclusions

The shredding of alkaline and saline Mignon-type spent batteries was studied using a laboratorial tip-cutter shredder. The size reduction was better achieved in the case of alkaline batteries being the main difference found in the larger size range -20+11.2 mm. Average particle diameters obtained were $d_{50} = 6.2$ and 9.1 mm, respectively for alkaline and saline batteries. Chemical elemental distribution with particle size showed that zinc concentration is almost constant while manganese decreases when particle size increases. Iron is almost totally present in large fractions

(between 5.6 and 20 mm). The separation of steel scrap by sieving of large size fragments was evaluated, being the size 5.6 mm considered the adequate sieve aperture to attain high recovery yields. About 96-99% of iron can be efficiently removed in gross fraction, but with substantial loss of zinc (40-71%) and also some manganese (28-59%), corresponding to the wet electrode particles aggregated with the steel scrap. Saline batteries have higher Zn and Mn losses in the gross materials when compared with alkaline batteries.

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