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Utilization of automotive shredder residues in a thermal process for recovery of manganese and zinc from zinc–carbon and alkaline spent batteries

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ABSTRACT

The aim of the study is the recovery by thermal treatment of manganese and zinc from a mixture of zinc–carbon and alkaline spent batteries, on the basis of the different phase change temperatures of the two metal-bearing phases. ASR (Automotive Shredder Residue), containing 68% of carbon, was added to the mixture to act as a reductant to metallic Zn of the zinc-bearing phases. The mixture was subsequently heated in different atmospheres (air, CO_2 and N_2) and at different temperatures (900 °C, 1000 °C and 1200 °C) and stoichiometric excess of ASR (300%, 600% and 900%). Characterization of the mixture and of the residues of thermal treatment was carried out by chemical analysis, TGA/DTA, SEM and XRD. The results show that recovery of 99% of zinc (grade 97%) is achieved at 1000 °C in N_2 with a stoichiometric excess of car-fluff of 900%. This product could be suitable for production of new batteries after refining by hydrometallurgical way. Recovery of Mn around 98% in the residue of the treatment is achieved at any temperature and atmosphere tested with a grade of 57% at 900% excess of car-fluff. This residue is enriched in manganese oxide and could be used in the production of iron–manganese alloys.

1. Introduction

Different metal values are contained in spent alkaline batteries and zinc–carbon batteries. Iron is present in the end-caps, in the alkaline batteries steel can and, in some cases, in the steel outer jacket of zinc–carbon batteries; copper and zinc are contained in the alkaline battery brass negative collector. These components can be preliminary and easily removed from spent batteries.

On the contrary, most of manganese and zinc are contained in the paste inside the batteries, so that a separation process of these two metals is needed for their recovery and recycling. These metals are the basis for the production of alkaline and zinc–carbon batteries which covers 90% of the European battery market. As a consequence, the increase in battery consumption causes both a more intense exploitation of zinc and manganese-bearing raw materials and a greater need of landfills for the disposal of spent batteries that are an environmental hazardous waste. In fact, spent batteries can be also a potential source of heavy metals in landfill leachate, especially manganese whose limit for groundwater is much lower than for zinc (Avraamides et al., 2006).

For these reasons, the Directive 2006/66 of the European Commission (Directive EC, 2006) has prohibited to landfill this type of spent batteries before their treatment; the batteries must be recycled to recover at least 50% (by average weight) of the valuable materials they contain. Moreover, the same European Directive requires the achievement of a minimum collection rate of 45% by September 2016.

The methodologies currently used to recover valuable metals from spent batteries, use preliminary physical methods of separation followed by pyro (Baba et al., 2009; U.S. Patent 7169206 B2, 2007) or hydrometallurgical treatment (Da Silva et al., 2010; De Souza and Tenorio, 2004; Gallegos et al., 2013; Ma et al., 2014; Salgado et al., 2003; Quintanilha et al., 2014; Xiao and Meng, 2009) to recover the metals under various forms. The main drawback of pyrometallurgical processes is the greater energy consumption than that needed for hydrometallurgical processes. However, most of the pyrometallurgical processes for the treatment of ferrous and non-ferrous metals are conducted in large metallurgical plants. These plants can accept wastes like the paste of the batteries, containing manganese and zinc, as a part of

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the common primary raw material feed without affecting the environmental impact and the quality of their products. In addition, the process can also profit of the energy produced by the combustion of graphite and plastics contained in the battery waste. Slag is also produced and sometimes can be taken as inert material. Hydrometallurgical plants are small-scale operations and are less energy consumers but have specific water pollution problems. Drawbacks and advantages of both types of processes must be considered case by case, taking into account plant localization, distance, collection of spent batteries and transport, all being factors that can affect the environment and the economic efficiency of the process. Nevertheless, hydrometallurgical plants allow the production, according to EN 1179 standard, of an electrolytic refined zinc of higher purity (99.995%) than that obtained by pyrometallurgical processes, and the former is suitable for battery production. This European Standard specifies the chemical composition and other requirements for SHG primary zinc and has set the following limits: Al < 10 mg kg^{-1}, Cd < 30 mg kg^{-1}, Cu < 10 mg kg^{-1}, Fe < 20 mg kg^{-1}, Pb < 30 mg kg^{-1}, Sn < 10 mg kg^{-1}, and the sum of the 6 metals <50 mg kg^{-1}. At present, there is no standard for zinc metal for the production of primary zinc batteries. In practice, zinc batteries are made of top quality zinc SHG that is tested by battery manufacturers. The major issue is corrosion and battery leakage caused by unwanted impurities such as Fe that is required to have a concentration below 3 mg kg^{-1} and not 20 mg kg^{-1} as required for SHG primary zinc.

Against this background, the zinc or zinc oxide produced by the pyrometallurgical route could be added to the feed of the final electrolytic step of a hydrometallurgical plant to reach the purity required for the production of new batteries.

Zn is present in the paste of battery both as elemental zinc and as zinc oxide (ZnO), while Mn is mainly present as Mn_3O_4 in the paste. Thermal desorption allows the separation of the two metals by taking advantage from different phase change temperatures that are 906 °C, the b.p. for Zn, which can be also attained by reduction of ZnO, and 1564 °C, the m.p. for Mn_3O_4 (Handbook CRC Press, 1980). Zn volatilizes during the thermal process that is carried out above its b.p. while Mn is left in the residue.

The reduction of ZnO to metallic zinc can be accomplished by the carbon contained in the zinc–carbon batteries of the spent battery waste, if they are present in sufficient quantity (Belardi et al., 2012) or by the carbon from different external sources. It should be highlighted that zinc–carbon batteries will go out of production within next years, as they are less efficient than alkaline batteries. As a consequence, the addition of carbon from an external source will be needed for performing the reduction of the zinc oxide.

In this study, ASR (Automotive Shredder Residue), also known as car-fluff, was utilized as the external carbon source. This waste is generated from the end of life vehicles after dismantling, shredding and sorting valuable ferrous and non-ferrous metals and it counts about 20–25% by weight of the vehicle's total weight. Car-fluff represents up to 10% by weight of the whole amount of the hazardous wastes produced per year in the European Union. This waste is a highly heterogeneous material, mainly composed of plastic, rubber/elastomer, metals, glass, textiles and other rubbles (Rossetti et al., 2006). Car-fluff contains dangerous substances and it is marked as a hazardous waste in the European Waste Catalogue (EWC) with the code 19 10 03 that is "fluff-light fraction and dust containing dangerous substances". This designation is a specific item of the general code 19.10 that is shredding of metal-containing wastes.

The aim of this paper is the recovery of manganese and zinc from a mixture of zinc–carbon and alkaline batteries by thermal desorption, comparing different atmospheres (air, carbon dioxide and nitrogen), different stoichiometric excesses of car-fluff (300%, 600% and 900%) and utilizing lower temperatures (900 °C, 1000 °C and 1200 °C) than those used in the current pyrometallurgical processes (U.S. Patent 7169206 B2, 2007). The desorption tests were carried out after having characterized the spent batteries (Belardi et al., 2011) and after having applied a physical process of separation (Belardi et al., 2012) for the removal of most iron and organic matters contained in the waste. A recent paper (Belardi et al., 2014) reports a similar thermal process but the external source of carbon was activated charcoal, pure grade, taken from the shelves of a chemical laboratory. In this case, the external source of carbon is a real hazardous waste as the car-fluff is. No application of car-fluff as a reductant agent was found in the literature being coke breeze the reductant generally used in pyrometallurgical plants.

2. Materials and methods

2.1. Material and chemicals

Characteristics of the zinc carbon and alkaline spent batteries are reported in previous papers (Belardi et al., 2011, 2014). Both types of spent batteries have not been separated from each other after collection, to simulate the feed of an industrial process; in fact, the separation between the two types of batteries is only feasible by visual inspection at a small scale but not at a large one with automatic separation methods. Full details of the wet preliminary physical treatment of the mix of batteries, to obtain a paste suitable for the successive thermal desorption, are reported on a previous paper (Belardi et al., 2014). During that treatment, the brass negative collectors of the alkaline batteries, were removed, and the chloride content was reduced by more than 90%, being 0.1% the amount left in the paste of battery. About 80% of the paste was passing at 750 μm, being 16% the material below 53 μm. Chemical analysis of the paste of batteries used for thermal desorption in Table 1. The sample destined to the thermal treatment contained 25.95% Zn, 33.25% Mn, 1.92% Fe, 6–8% C, as main components and amounts of other elements less than 1%. Mercury was present below 1 mg kg^{-1}, and this assured that the batteries were produced according to the European rules that fix at 5 mg kg^{-1} the limit for this metal. Car-fluff was supplied by a recycling company that had removed glass and inert materials from the waste. Composition of car-fluff is reported in Table 2. Before preparation of the mixes with the paste of batteries, the fluff was comminuted to below 1 mm in order to increase the specific surface and to obtain a material as homogenous as possible. This way, each addition of fluff, had about the same chemical composition.

Table 1
Chemical composition of the paste of batteries used for thermal desorption of zinc.

Component	% dry solid
Mn	33.25 ± 0.02
Zn	25.95 ± 0.02
Fe_2O_3	1.92 ± 0.001
CaO	0.35
SiO_2	0.33
MgO	0.22
K_2O	0.21
Na_2O	0.20
TiO_2	0.18
BaO	0.14
Al_2O_3	0.10
CuO	0.05
P_2O_5	0.02
V_2O_5	0.02
C	6–8
LOI (1000 °C)	13.15 ± 0.01

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