



# Reductive acid leaching of spent zinc–carbon batteries and oxidative precipitation of Mn–Zn ferrite nanoparticles

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## ABSTRACT

The non-magnetic 8-mesh undersize material obtained by crushing, magnetic separation and sieving of spent zinc–carbon batteries assayed 23.9% Mn, 14.9% Zn, and 4% Fe. Reductive acid leaching of this material at a solid/liquid ratio of 1:10, and 60 °C with 2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 0.39 mol H<sub>2</sub>O<sub>2</sub> extracted 97.9% Mn, 98.0% Zn and 55.2% Fe after 60 min. The leach liquor composition was then adjusted to a Mn:Zn:Fe molar ratio of 1:1:4 suitable for producing MnZnFe<sub>4</sub>O<sub>8</sub> ferrite powder by adding Mn(II), Zn(II) and Fe(II) sulfates. The effect of pH in the range pH 5–12 on the precipitation of Mn–Zn ferrite powder was investigated over 60 min using O<sub>2</sub> gas flow rate of 1.3 dm<sup>3</sup> min<sup>-1</sup> at 80 °C. The precipitated Mn–Zn ferrite at pH 12 were 20 nm particles that had a spinel structure. The saturation magnetizations of Mn–Zn ferrite powder (Mn<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub>) were determined to be 39–91 emu/g with various zinc contents (x=0.2–0.8).

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## 1. Introduction

The recovery of industrially useful materials and metals from various secondary sources has been an important issue in Korea since its natural resources are limited and its need for the strategic metals are on the rise. The domestic annual demand for manganese metal is approximately 700,000 ton, which are consumed in the manufacture of batteries, nonferrous alloys, and steel making. Zinc metal is used as plating material, coating material, and alloying element. In 2005 alone, 1,150,000 ton of zinc ore were imported, whereas only 30 tons of zinc ore were excavated domestically and domestic market of Mn–Zn ferrite is worth nearly US\$320 M.

More than a billion spent batteries are generated as wastes annually in Korea. To solve environmental problems and to conserve natural resources, recycling technology for the waste batteries is being developed (Vatistas et al., 2001; Xi et al., 2004; Freitas and Depietre, 2004; Shin et al., 2007). In 2003, the producer deposit system was replaced by the extended producer responsibility system (EPR), which has imposed waste recycling obligations on producers or importers of high waste-generating products and packaging materials. Spent batteries in the EPR list include silver-oxide batteries, lithium primary batteries and nickel–cadmium batteries. Lithium ion batteries along with spent mobile phones were added into the EPR list in the year 2005. Zinc–carbon and alkaline–manganese batteries were also

included in the EPR list in 2008. So, most of spent battery types generated in Korea are currently included in the recycling list.

Since 1996, all alkaline–manganese and zinc–carbon batteries manufactured in Korea have not contained any added mercury because mercury amalgamated with zinc has been replaced with first lead and lead–indium and next with gallium and aluminum–gallium. Therefore, it is expected that the landfill disposal of alkaline–manganese and zinc–carbon batteries does not directly pose a significant health or environmental risk. Since cobalt, manganese, zinc, and nickel as strategic metals are accumulating domestically; the recycling industry could be stimulated by recovering metal values from spent batteries; thereby solving potential environmental problems. Recycling processes for spent zinc–carbon and alkaline–manganese batteries should be developed to achieve environmental conservation as well as the effective utility of resources. In the present work, experiments were carried out to synthesize high purity Mn–Zn ferrite powder (MnZnFe<sub>4</sub>O<sub>8</sub>) used as a transformer magnetic material using reductive sulfuric acid leaching of the non-magnetic fraction of crushed spent zinc–carbon batteries and oxidative co-precipitation of the mixed metals.

## 2. Experimental procedure

### 2.1. Sample preparation

Fig. 1 shows a schematic diagram of a typical zinc–carbon battery. The spent zinc–carbon batteries are composed of Zn, MnO<sub>2</sub>, as well as ZnO and Mn<sub>2</sub>O<sub>3</sub> produced from the discharging reaction (Bernardes

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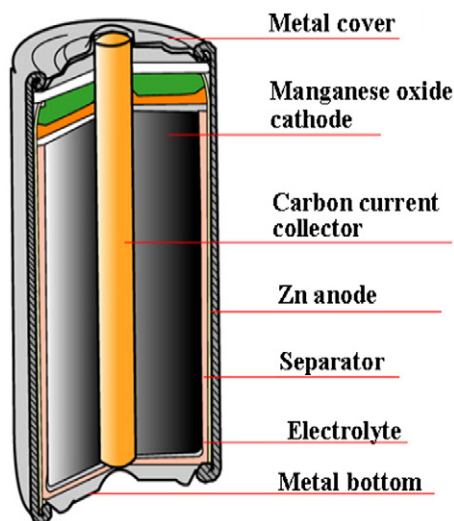


Fig. 1. Schematic diagram of a typical zinc-carbon battery cross section.

et al., 2004; Park et al., 2006). They also contain magnetic materials, small amounts of carbon, plastics, and electrolyte. Mechanical processing of the spent batteries was conducted to yield an undersize non-magnetic fraction with a high composition of zinc and manganese. The procedure included crushing, sieving, magnetic separation, fine crushing, and classification in sequence (Park et al., 2006; Kim et al., 2008). Thus, the physical treatment applied herein yielded three kinds of fractions, namely magnetic material and non-magnetic 8-mesh (2.46 mm) oversize and undersize. The composition of the 8-mesh undersize, used as a feedstock for subsequent experiments, determined by atomic absorption spectrophotometry (AAS) was: 23.9% Mn, 14.9% Zn, and 4% Fe.

2.2. Reductive leaching and oxidative precipitation

The production of Mn-Zn ferrite powder from the 8-mesh undersize included two stages: (i) reductive acid leaching, and (ii) oxidative alkaline co-precipitation (Fig. 2). At first, a sulfuric acid leaching experiment was carried out for 60 min using 2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 0.39 mol H<sub>2</sub>O<sub>2</sub> at 60 °C and a solid/liquid ratio of 1:10 with an agitation speed of 200 rpm. The leach liquor was filtered and the

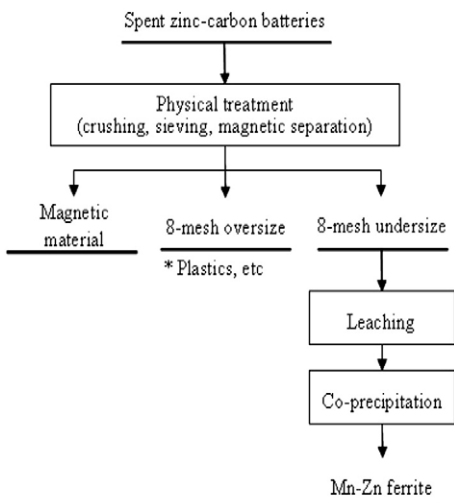


Fig. 2. Flow sheet for producing Mn-Zn ferrite powder from spent zinc-carbon batteries.

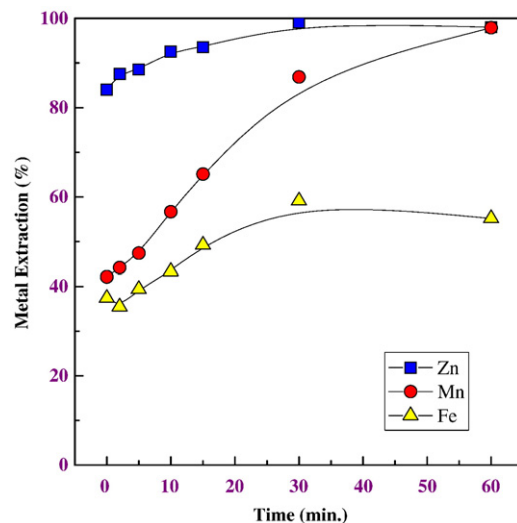


Fig. 3. Mn, Zn, and Fe extractions as a function of time in sulfuric acid leaching of the 8 mesh undersize fraction.

concentrations of Zn, Mn, and Fe in the liquor and residue were analyzed by AAS.

To synthesize Mn-Zn ferrite powder, a 50 cm<sup>3</sup> sample of the leach liquor was diluted to 700 dm<sup>3</sup> to prepare a feedstock solution containing the required Mn: Zn: Fe molar ratio of 1:1:4 by the addition of 2.91 g zinc sulfate (ZnSO<sub>4</sub>·7H<sub>2</sub>O), and 23.15 g iron sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O). The precipitation was carried out at different pH values to examine the most effective pH for complete precipitation. The leach liquor at the adjusted molar ratio was placed in the reactor and the precipitation was allowed to take place over 60 min at 80 °C, 200 rpm, under O<sub>2</sub> gas flow rate at 1.3 dm<sup>3</sup> min<sup>-1</sup>. After filtering, the co-precipitate was washed thoroughly with distilled water to neutral pH and dried at 100 °C for 12 h to obtain ferrite powder.

2.3. Characterization of Mn-Zn ferrite

The precipitate was filtered and dried for 3 h at 200 °C. The chemical composition of the ferrite powder was determined by AAS (Spectra AA-400, Varian); and the morphology was examined using a scanning electron microscope (JSM-6380LA, JEOL) and a transmission electron microscope (JSM-6380LA, JEOL, Japan). The preferred crystal orientation and magnetic property of the ferrite were determined

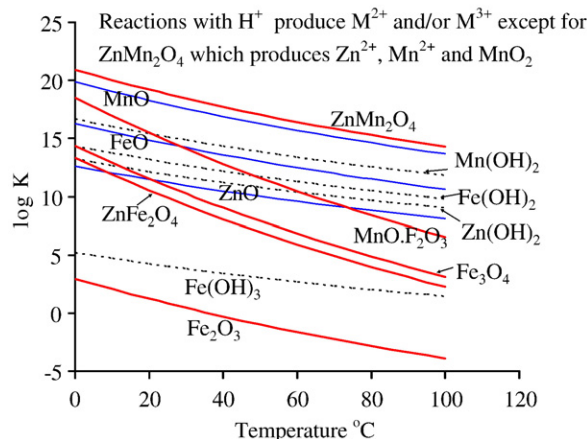


Fig. 4. Effect of temperature on equilibrium constants for the dissolution of oxides (data from HSC 6.1).

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