Journal of Hazardous Materials B127 (2005) 244–248

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Short communication

The dissolution mechanism of cathodic active materials of spent Zn–Mn batteries in HCl

Yunqing Li *, Guoxi Xi

College of Chemistry and Environmental Science, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Xinxiang 453007, PR China

Received 8 April 2005; received in revised form 5 July 2005; accepted 17 July 2005
Available online 26 August 2005

Abstract

The cathodic active materials of spent Zn–Mn batteries are complicated. The majority materials that they contain are $Mn(OH)_2$, Mn_2O_4, λ-Mn_2O_2, $ZnMn_2O_4$, $Zn(NH_3)_2Cl_2$, $[Zn(OH)_2]_4 \cdot ZnCl_2$, etc. Dissolving these kinds of materials is important to the environmental pollution control and materials recycle. In present paper we investigated the dissolution mechanism of the cathodic active materials in HCl by testing the factors that can influence the dissolution procedure, including temperature, time, and the concentration of HCl and H_2O_2. Our results showed that both neutralization and oxidation–reduction reactions occurred in the dissolution process, and that H_2O_2 had a great effect on the dissolution efficiency.

Keywords: Spent Zn–Mn batteries; Cathodic active materials; Dissolution mechanism

1. Introduction

Due to the convenience and lower price, batteries, especially Zn–Mn batteries, have been being used widely for various purposes. This popular usage results in a quick increase of accumulation of waste batteries. Although the so-called "mercury-free batteries" has been used for decades [1,2], the waste batteries still caused a serious concern due to their toxicity, abundance and permanence in the environment. Study on recycling spent batteries is necessary and imperative.

Numerous studies on recycling spent batteries have been done in the past years, which can be summarized as pyrometallurgy and hydrometallurgy. Pyrometallurgy means that the spent batteries should just be recycled in high temperature furnaces. Pace et al. [3] recycled spent dry batteries by heating them to the temperature over 800 °C. The residue content of the most toxic metals in the treated waste is lowered below 100 mg/kg. Toita et al. [4] and Krebs [5] tried in different ways. They heated spent Zn–Mn batteries in an oxidation furnace or a melting furnace, and obtained high purity metals after a series of treatment. Other pyrometallurgical methods used to treat spent batteries were hammer mill grinding, magnetic separation, size separation, specific gravity separation, etc. [6]. The disadvantages of pyrometallurgy are high cost, spending more energy and complicated operations. The hydrometallurgy means that a solvent must be used in the recycling process. One of the methods used is to obtain manganese zinc ferrite by treating waste Zn–Mn dry cell though dissolving, co-precipitating and oxidizing procedures [7]. Another method [8] is to obtain pure $ZnCl_2$ and MnO_2 by water washing, HCl dissolving and heating. Waste dry cells were dissolved in basic ammonium carbonate solution to recover Zinc [9].

Various industrial recycling processes have been proposed, and some of them are being operated, for example, Batrec AG (in Switzerland) operates an industrial plant for recycling used dry batteries with a production capacity of 3200 tonnes per year [5]. Batenus process operates a plant in Germany with a capacity of 7500 tonnes per year [10]. But usually they recycle any type of spent dry batteries just in almost the same way, thus they are not specific or efficient.

* Corresponding author. Tel.: +86 373 3326335; fax: +86 373 3326336.
E-mail address: lyqldx@yahoo.com.cn (Y. Li).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.07.024

There is only one specific recovery process operated in USA. They recover metals from the exhausted nickel–cadmium, –iron and –metal hydride batteries. The capacity of this plant is about 2300 tonnes per year [11]. Due to the limitation of the industrial recycling plant, the spent dry batteries are mainly disposed as domestic refuse in most countries, especially in developing countries. Exploring economic recycling process will be significant for the environmental pollution control. Because Zn–Mn batteries are widely used, we try to find a better way to recover used Zn–Mn batteries by combining the advantages of both pyrometallurgy and hydrometallurgy. The key steps of hydrometallurgy are to dissolve, extract, and recover the useful components. Therefore, we intend to study the dissolution mechanism of the cathodic active materials of Zn–Mn batteries in HCl.

The anode of Zn–Mn battery is mainly Zn, which can be easily dissolved in HCl. Its cathodic active materials mainly contain $Mn(OH)_2$, Mn_2O_4, γ-Mn_2O_2, $ZnMn_2O_4$, $Zn(NH_3)_2Cl_2$, $[Zn(OH)_2]_4 \cdot ZnCl_2$ and a little natural mineral materials [12,13]. The specific composition depends on some characteristics of the batteries such as discharge state, stocking conditions, etc. Our previous work studied the dissolving conditions in HCl, but the dissolution mechanism has not been illustrated. In present paper, we investigated the dissolution mechanism of cathodic active materials in HCl. We found that both neutralization and oxidation–reduction reactions occurred in the dissolution process and H_2O_2 could have a great effect on the dissolution efficiency. These results provided some useful basic data for practical study in the future.

2. Experimental

2.1. Materials and methods

Analytical grade HCl and H_2O_2 were purchased from Beijing Chemical Plant (China). Zn–Mn batteries used in this experiment were size R20 Zhonghua brand battery made in Xinxiang Battery Plant (Henan, China).

The cathodic active materials were taken out of the splitting spent Zn–Mn batteries, roasted at 300 °C for 2 h in a furnace of the muffle type (Tianjin Dongya Electric Oven Plant, China), milled in a motar, and sieved with a 315-micron-mesh sieve. The final products, samples, were put into an exsiccator.

The schematic of experimental apparatus was shown in Fig. 1. Certain amount of HCl was weighed in a beaker and heated to a certain temperature in a super constant temperature tank (Shanghai Instrument Co., China), and then the sample and H_2O_2 were added with stirring.

After cooling down to room temperature, the solution was filtered decompressively with G_3 core glass crucible. The filter residue then was dried to a constant weight at 100 ± 2 °C. The filtrate was analyzed to measure Zn and Mn by Z-5000 atomic absorption spectrophotometer (HITACHI, Japan). The dissolution ratio was calculated according to the following form:

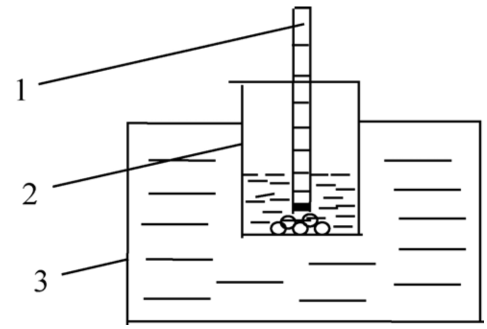

Fig. 1. Schematic of experimental apparatus: 1, thermometer; 2, beaker; 3, super constant temperature oven.

$$\phi = \frac{G - m}{G} \times 100 \tag{1}$$

where ϕ stands for the dissolution ratio of sample (%), G and m represent the mass of sample (g) and the filter residue after being dried (g), respectively.

2.2. Theory analysis

The cathodic active materials of the size R20 Zhonghua brand battery mainly contains $Mn(OH)_2$, MnO_2, γ-Mn_2O_2, $ZnMn_2O_4$, $Zn(NH_3)_2Cl_2$, $[Zn(OH)_2]_4 \cdot ZnCl_2$, and a few natural mineral materials. When put into HCl, $Zn(NH_3)_2Cl_2$, and $[Zn(OH)_2]]_4 \cdot ZnCl_2$ in the active materials should react with HCl as follows:

$$Zn(NH_3)_2Cl_2 = [Zn(NH_3)_2]^{2+} + 2Cl^- \tag{2}$$

$$[Zn(NH_3)_2]^{2+} + 2H^+ = Zn^{2+} + 2NH_4{}^+ \tag{3}$$

$$[Zn(OH)_2]_4 \cdot ZnCl_2 = 5Zn^{2+} + 2Cl^- + 8OH^- \tag{4}$$

$$OH^- + H^+ = H_2O \tag{5}$$

Then MnO(OH), MnO, and $ZnMn_2O_4$, which are more difficult to dissolve in water, would react with HCl as follows:

$$MnO + 2H^+ = Mn^{2+} + H_2O \tag{6}$$

$$2MnOOH + 2H^+ = Mn^{2+} + MnO_2 + 2H_2O \tag{7}$$

$$ZnMn_2O_4 + 4H^+ = Zn^{2+} + Mn^{2+} + 2H_2O + MnO_2 \tag{8}$$

Under appropriate conditions, Mn_2O_4 could react with HCl according to the following equation:

$$MnO_2 + 4HCl = Mn^{2+} + 2Cl_2\uparrow + 2H_2O \tag{9}$$

From analysis above, we can conclude that both neutralization reactions and oxidation–reduction reactions occurred in the dissolution process. Many reactions are heterogeneous phase, therefore, the process must be very complicated and the reaction time would be very long.