Metal separation from mixed types of batteries using selective precipitation and liquid–liquid extraction techniques

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ABSTRACT

The purpose of this paper is to study metal separation from a sample composed of a mixture of the main types of spent household batteries, using a hydrometallurgical route, comparing selective precipitation and liquid–liquid extraction separation techniques. The preparation of the solution consisted of: grinding the waste of mixed batteries, reduction and volatile metals elimination using electric furnace and acid leaching. From this solution two different routes were studied: selective precipitation with sodium hydroxide and liquid–liquid extraction using Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphoric acid] as extracting agent. The best results were obtained from liquid–liquid extraction in which Zn had a 99% extraction rate at pH 2.5. More than 95% Fe was extracted at pH 7.0, the same pH at which more than 90% Ce was extracted. About 88% Mn, Cr and Co was extracted at this pH. At pH 3.0, more than 85% Ni was extracted, and at pH 3.5 more than 80% of Cd and La was extracted.

1. Introduction

Currently, as a result of technological innovations, the number of portable electronic devices such as laptop computers, CD-players, walkmans, and mobile phones, are increasingly used worldwide, resulting in an increasing demand for batteries. Secondary battery systems, such as nickel–cadmium (NiCd), nickel-metal hydride (NiMH) or lithium–ion batteries have been developed for such gadgets.

According to guidelines published in various countries, the appropriate outcome and destination for spent batteries may involve methods such as landfill deposition, stabilization by incineration (with some restrictions) and/or recycling processes (Bernardes et al., 2004). Safe disposal in landfills or spent-battery stabilization processes become increasingly expensive because of increasing amounts of waste as well as limited sanitary landfill storage capacity and/or special waste dumpsites. Incineration of batteries is restricted by environmental legislation as it can release mercury, cadmium and dioxins to the atmosphere (Bernardes et al., 2004). Therefore, spent-battery recycling is extremely important as it benefits future generations and preserves raw materials.

The main types of batteries currently used are zinc–carbon (Zn–C), alkaline, nickel–cadmium (NiCd), nickel–metal hydride (NiMH) and lithium–ion (Li–ion). Some batteries such as NiCd and Pb–acid contain toxic metals such as cadmium and lead which are highly toxic and should be properly discarded (Zhao et al., 2008).

Cadmium is a relatively rare metal and is distributed in the Earth's crust at a concentration of approximately 0.08–0.5 ppm (Kumbasar, 2008).

NiMH batteries have a high energy storage capacity combined with an ecologically friendly composition compared to cadmium contained in Ni–Cd batteries (Muller and Friedrich, 2006). Typically the most important elements composing NiMH batteries are nickel, cobalt and rare earth metals (REM). Ni–MH positive electrode batteries are made of a porous Ni plate with nickel hydroxide. The negative electrode consists of REM–Ni–Co alloys on a metal-mesh substrate (Muller and Friedrich, 2006). Lupi and Pilone (2002) proposed a route to produce Ni–Co alloys from NiMH batteries through an electrowinning process.

Zinc–carbon batteries contain zinc, manganese dioxide, steel (Avraamides et al., 2006), and also a carbon rod cathode in contact with a moist paste of MnO_2, NH_4Cl and $ZnCl_2$ with an acid electrolyte and zinc anode.

Veloso et al. (2005) proposed a hydrometallurgical route to recover zinc and manganese from discarded alkaline batteries in which the preliminary treatment of batteries consisted of the following sequential steps: sorting, dismantling, grinding and leaching. In neutral leaching, a black dried powder was treated with different volumes of distilled water, at solid/liquid ratio of $1/20$ mg L^{-1} which showed that dissolution of potassium in water is practically instantaneous, with a rapid increase in the pH solution to values of approximately 11–12 in the first 30 s. It was also verified that nearly 100% of potassium was dissolved within 5 min.

Using acid leaching, Avraamides et al. (2006) studied another route to leach spent zinc–carbon-battery scrap, in which crushed materials were subjected to magnetic separation followed by

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hydrometallurgical treatment of the non-magnetic material to recover zinc and manganese oxides. Leaching with 2 mol L^{-1} sulfuric acid in the presence of hydrogen peroxide recovered 93% Zn and 82% Mn at 25 °C. Alkaline leaching with 6 mol L^{-1} NaOH recovered 80% zinc. The study showed that 90% zinc and manganese can be leached out within 20–30 min at 30 °C using sulfuric acid.

The consumption of batteries in the USA and Europe is estimated at 8 billion units per year. In Japan, roughly 6 billion batteries were produced in 2004, while almost 1 billion units are consumed every year in Brazil (Xu et al., 2008).

In most lithium–ion systems, the cathode includes $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$. The Li–ion system contains a toxic and flammable electrolyte consisting of lithium salts ($LiClO_4$, $LiPF_6$), organic chemicals and plastics in proportions of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemicals and 7% plastics (Xu et al., 2008).

Dorella and Mansur (2007) studied a method to recycle Li–ion batteries, in which iron scraps and plastic separation was performed manually as well as the anode/cathode separation. In this work, leaching was carried out with sulfuric acid in an oxidizing environment to transfer metals from the residue to an aqueous solution; precipitation with NH_4OH was made to separate aluminum, and liquid–liquid extraction with Cyanex 272, to separate cobalt from lithium, resulting in a concentrated metal solution (about 63 g L^{-1} of cobalt) quite adequate for electrowinning.

In the present study we compare two methods for selective separation of metals in a liquor from a sample composed of a mixture of the main types of spent household batteries: selective precipitation and liquid–liquid extraction.

2. Materials and methods

2.1. Preliminary treatment

The material used in this study was derived from a mixture of different types of spent batteries. The composition of the mixture was based on the battery waste collected in one collection point for 1 month by a non-governmental organization which collects used batteries in various sites in Sao Paulo, Brazil. To quantify the different types of batteries present in studied material the batteries were manually opened and their different components were separated, classified and weighted. Table 1 shows the composition of the material studied regarding the battery type.

The material was ground, briquetted and submitted to the reduction tests in which the material was treated at 1000 °C for 4 h under inert atmosphere to eliminate volatile metals present in the charge, such as cadmium, zinc and mercury and to reduce the manganese oxides to MnO, which is soluble in sulfuric acid. 1000 °C was chosen because it is biggest to the volatilization temperatures of Cd, Zn and Hg and reduction temperature of the oxide manganese to MnO. The use of this temperature favors the elimination of mercury contained in the Zn–Mn dry batteries, and after mercury decontamination is possible to recoup zinc for distillation (Oliveira et al., 2001), and cadmium present in Ni–Cd batteries can be recouped by distillation (Masamoto et al., 1993; Delisle et al., 1995). Magnetic separation was then performed in material that

Table 1
Composition of the representative lot prepared for the study.

Battery type	Weight (%)
Zn–C alkaline	60
Zn–C dry cell	36
NiCd	1.9
NiMH	1.4
Li–ion	0.7

remained in the crucible after heating. The non-magnetic portion of black powder after reduction tests was leached in sulfuric acid, and the metal concentration of liquor was determined by inductively coupled plasma optical emission spectrometry using a Varian ICP–OES spectrometer.

Leaching in sulfuric acid was performed in the non-magnetic portion. Sulfuric acid has been used for leaching by various researchers (Havlik et al., 2005; Padilla et al., 2005). Although, sulfuric acid is not as effective as stronger acids like nitric acid and hydrochloric acid (Copur, 2002), it is preferred overall other leaching reagents in terms of cost, environmental friendliness, fewer corrosion problems, and ease of its regeneration during electrowinning (Biswas and Davenport, 1980).

All tests were carried out at room temperature, in the relation of solid/liquid (S/L = 1/10 g mL^{-1}) in H_2SO_4 1 mol L^{-1} for 24 h.

2.2. Selective precipitation

Selective precipitation experiments were carried out at room temperature with the pH of the monitoring solution. In these tests, a basic solution of NaOH 2 mol L^{-1} was added very slowly to the liquor obtained in the sulfuric acid leaching step to raise the pH of the aqueous solution. Samples were withdrawn at pH 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.2 and 6.0 and filtered in a membrane. The metal content in the aqueous phases was determined by ICP/OES. The aqueous solution pH was monitored using a digital Digimed DM 22 pH meter.

The effect of hydrogen peroxide (H_2O_2) was studied in selective precipitation, and the results were compared with selective precipitation without H_2O_2.

2.3. Study of metal concentration influence on the yield precipitation (w/w)

Different concentrations of $MnSO_4$ solution (0.2–38 g L^{-1}) were prepared; pH was adjusted to 8.0 with NaOH to precipitate $Mn(OH)_2$. After filtration of each precipitate, the solutions were analyzed by ICP–OES. The pH chosen was sufficiently high enough to ensure that pH of manganese precipitation in the ideal pressure conditions and temperature was exceeded.

2.4. Solvent extraction

Liquid–liquid extraction is a technique generally used to separate metals in aqueous solution in which a solution (in this work, the leach liquor) is brought into contact with a solvent, so that it can transfer the metal ions dissolved in the aqueous phase to the organic phase (each one at a specific pH) and then by re-extraction, transfer them back to another aqueous phase, one at a time. The commercial extractant employed was Cyanex 272, containing as the active component bis (2,4,4-tri-methylpenthyl) phosphoric acid. The concentration in organic solution was 0.6 mol L^{-1}. The diluent used was kerosene. The pH adjustment was performed by addition of a sodium hydroxide concentrated solution. The extractions were made in pHs 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; 4.5; 5.0; 5.5; 6.0; 6.5 and 7.0 with 3 contacts of 20 min each one.

3. Results and discussion

3.1. Leaching in sulfuric acid

The non-magnetic portion of black powder composition after reduction tests was determined by ICP/OES, the analysis are made in triplicate and the results and its Relative Standard Deviations are shown in Table 2.