

Short Communication

Hydrometallurgical recovery process for nickel–cadmium spent batteries

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Abstract

The most recent literature on the treatment of nickel–cadmium spent batteries often describes mixed pyro- and hydrometallurgical processes with different options (precipitation, electrolysis, solvent extraction) for the recovery of the metal. The present work shows a completely hydrometallurgical process in which electrode powder is mechanically separated from the external case and the metal supports, and afterwards, the powder is leached with acid and then electrolyzed. It was thus possible to recover cadmium with 1.2% of nickel; nickel was finally precipitated as carbonate, containing less than 0.5% of cadmium.

Keywords: Nickel–cadmium batteries; Nickel; Cadmium; Recovery; Spent batteries

1. Introduction

Among the small household batteries, rechargeable nickel–cadmium batteries tend to cover 10% of the market; the estimated consumption in the year 2000 will be approximately 1000 g per person per year, at least in Western Europe. This estimation might be lower in the light of the marketing of a new battery type, the rechargeable alkaline manganese battery [1,2].

Nickel–cadmium batteries, in addition to their normal application in radios, calculators, torches, etc., are also assembled in battery-packs in videocameras, small household appliances, and cordless tools. A pack may supply 9 V.

Cadmium, considered as one of the most toxic metals, cannot be thrown away indiscriminately into the environment; studies have been carried out to evaluate its toxic effects on human beings [3]. Cadmium in the municipal solid waste will come largely from nickel–cadmium batteries [4,5].

In a previous work, the electrochemical recovery of cadmium from a synthetic solution containing 2000 ppm of the metal has been described [6], and in 1992, Bartolozzi and Magnani [7] reviewed pyrometallurgical processes in order to recover cadmium and nickel from spent batteries, mainly published in patents.

More recently, three kinds of spent nickel–cadmium batteries were considered and some preliminary ex-

periments were carried out in order to acquire information on possible separation of cadmium from nickel by cadmium electrodeposition [8].

In this work, the literature has been updated and a hydrometallurgical process has been developed in order to recover nickel and cadmium from a typical mix of batteries available on the market by chemical and electrochemical methods.

2. Literature review

2.1. 1991

Agh et al. [9] patented a process in which leaching of the electrode paste is followed by two extractions with organic solvents, the first one for nickel, and the second one for cadmium, finally giving the hydroxides of these two metals.

Yu et al. [10] described a calcination process in order to obtain the oxides of the two metals, which were selectively leached, and then CdCO_3 and NiSO_4 were precipitated.

Laszlo et al. [11] suggested an acidic leaching followed by cadmium cementation.

2.2. 1992

Van Erkel [12] patented a process starting with an acidic treatment of shredded batteries; after filtration, cadmium was extracted from this solution and finally electrolyzed; nickel was electrolyzed or precipitated as nickel hydroxide.

Xue et al. [13] proposed a method with initial acid leaching followed by precipitation of iron and manganese hydroxides; nickel was precipitated as a double salt at first, and finally recovered as nickel hydroxide. Cadmium was precipitated as carbonate. A plant capable to recover five tons of cadmium per year has been planned.

Gunjishima et al. [14] patented a procedure in which batteries were heated at 500 °C to remove volatile components; then, a combustion was performed to recover cadmium, at 900 °C in a non-oxidizing atmosphere.

Sun et al. [15] described a process of electrodic paste reduction using coal at high pressure and temperature; cadmium was then recovered by distillation.

Sakata et al. [16] patented a process for evaporating cadmium from small size spent batteries with a special furnace.

2.3. 1993

Gunjishima et al. [17] patented a process in which spent batteries were heated at 200 °C in a vegetable oil in order to remove the external polymer, then cadmium was recovered by vaporization at 1000 °C.

Plieth and Stambach [18] reviewed the economical and environmental aspects of recycling dry batteries, including nickel–cadmium batteries.

Salami [19] patented a process in which batteries were cooled using liquid nitrogen, then ground and the components separated in several steps.

Gunjishima et al. [20] patented a two-stage pyrometallurgical process for spent nickel–cadmium batteries; the first stage, in a non-oxidizing atmosphere at 500 °C, to remove plastic cases, and the second stage, at 900 °C, in order to recover the cadmium.

Sasaki et al. [21] described a method in which cadmium can be volatilized from spent sealed nickel–cadmium batteries by distillation at a temperature higher than 900 °C. The residue was an iron–nickel alloy with a very low cadmium content.

2.4. 1994

Alavi and Salami [22] patented a process in which the spent batteries were crushed and the different fractions separated magnetically and by air separation. The magnetic portion was scoured and washed to obtain a smeltable iron–nickel mixture. The fine fraction was dissolved in diluted acid and the metals extracted selectively.

Delisle et al. [23] described a process in which shredded batteries were heated at 1000 °C in a furnace containing coke. The vaporized cadmium was condensed and the residue containing nickel was processed by conventional methods.

2. Experimental

A set of nine batteries of different brands were examined; their structure is given in Fig. 1; their total weight is 400 g.

These batteries were demolished, producing paper and plastic (2 wt.%), metal (iron) (28 wt.%), and rolled electrodes (70 wt.%).

The electrode material had a water content of 4.4 wt.%. Paper and plastic resulted from external coatings, and the metal (iron) from the external case; the electrode material consisted of two metallic nets or bands, supporting the active substances, and a polymeric separation membrane.

The electrode material, dried at 105 °C, was separated by mechanical treatment, resulting in: metal (iron) (20 wt.%) a grey electrodic powder (74 wt.%), and a membrane (6 wt.%).

Several samples of the grey powder were analysed. Each sample (200 mg) was leached with a mixture of sulfuric and nitric acids or sulfuric acid and hydrogen peroxide until complete solubilization. The results evidenced that the material was not homogeneous.

A set of six analyses gave the following average values: cadmium (34.3 wt.%) and nickel (34 wt.%), referring to the dry powder. Dissolved metals were determined by atomic absorption spectrophotometry. The soluble salts in the powder were 6.2 wt.%.

3. Leaching and electrolysis

A sample of 19.867 g of dried powder was treated with a solution of 30 ml of concentrated sulfuric acid (32 wt.%), 180 ml of distilled water, and 15 ml of 32%

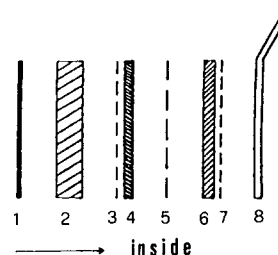


Fig. 1. Exploded view of a nickel–cadmium battery. (1) external plastic; (2) iron case; (3) metal foil for cathode support; (4) cathode; (5) membrane; (6) anode; (7) metal foil for anode support, and (8) conductor.

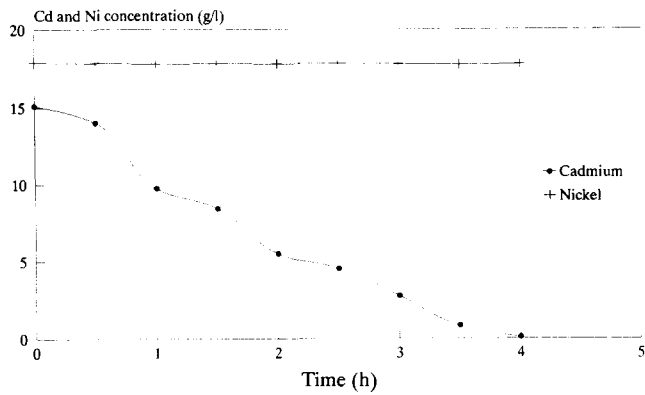


Fig. 2. Cadmium and nickel in solution during electrolysis at 500 mA.

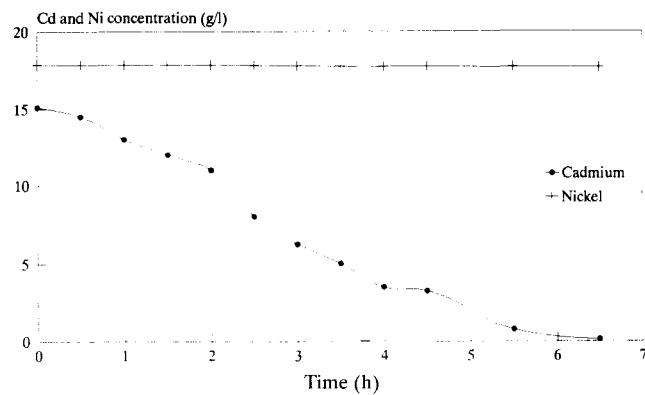


Fig. 3. Cadmium and nickel in solution during electrolysis at 300 mA.

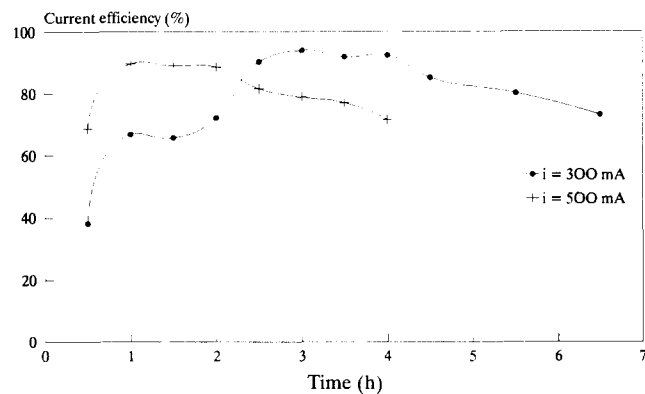


Fig. 4. Current efficiency for cadmium deposition vs. time.

hydrogen peroxide, under agitation for 1 h at 60 °C. After filtration, a grey residue (0.345 g) and a green solution (235 ml) with pH=0.3 were obtained. The pH increased up to pH=4 by adding 10 M NaOH and then up to pH=5.0 by adding 32% ammonia; thereupon, after heating for 10 min at 70 °C, iron hydroxide was precipitated. The final solution (302 ml) had a specific conductivity 11.5 mS cm⁻¹.

The volume was brought to 400 ml and the solution divided into two equal parts. Each part was subjected to electrolysis.

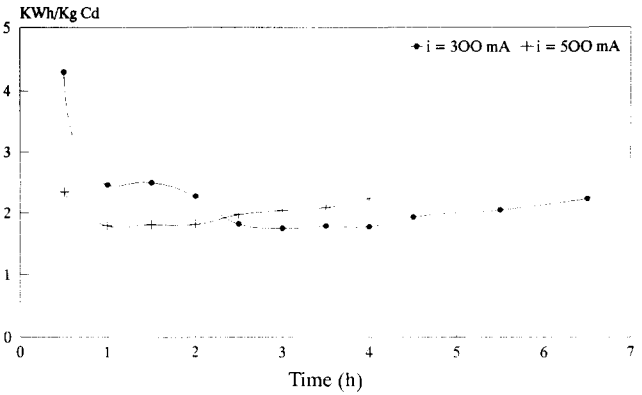


Fig. 5. Energy consumption for cadmium deposition vs. time.

The first electrolysis was run in a stirred batch; the constant current of 500 mA was supplied by a galvanostat. The cathode was a stainless-steel net of 6 cm² in area, the anode was a platinum net also of 6 cm², the inter-electrode distance was 30 mm. The experiment lasted for 4 h, the temperature was 51 °C and the cell voltage, which was almost constant, was 3.4 V. The cathodic potential decreased from -880 to -950 mV versus saturated calomel electrode, probably due to the dendritic nature of the deposit. Fig. 2 shows cadmium and nickel ion concentration versus time. 3.00 g of cadmium was actually recovered at the electrode, the deposit contained 1.2% of nickel.

The second electrolysis was carried out under the same conditions, but at a constant current of 300 mA. The cell voltage was 3.5 V, almost constant during the experiment that lasted for 6.5 h. The cathodic potential decreased from -940 to -980 mV versus saturated calomel electrode. 2.99 g of cadmium were recovered at the electrode, and contained 1.2% of nickel. Fig. 3 shows cadmium and nickel concentrations versus time, Figs. 4 and 5 compare current efficiency and energy consumption versus time during the two electrolyses.

4. Nickel precipitated as nickel carbonate

The solution from the second electrolysis (200 ml, pH = 1.3), contained ~3.5 g of nickel; its pH was brought to 7 with concentrated NaOH. Then 8 g of Na₂CO₃ were added, the pH became 8.5. A white-green precipitate was obtained, which became green after washing, resulting in NiCO₃ with 0.4 wt.% cadmium. The resulting solution contained 25 mg of nickel and 0.2 mg of cadmium.

5. Conclusions

The proposed process is completely hydrometallurgical and very simple, merely consisting of:

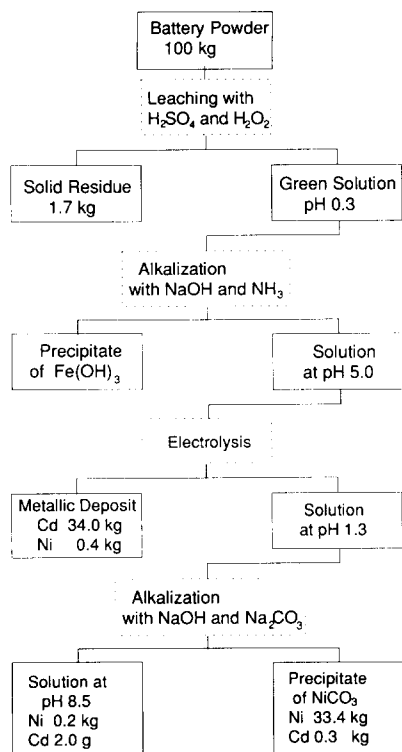


Fig. 6. Flow-sheet for the recovery of cadmium and nickel from spent batteries.

- mechanical separation of the electrode powder from the external case and metal supports
- leaching of the powder at moderate temperature and acidity
- alkalinization to precipitate iron
- electrodeposition of cadmium
- precipitation of nickel as carbonate

Both cadmium and NiCO_3 recovered were of good purity. Tests were made at currents of 300 and 500 mA. Cadmium recovery of about 99% was obtained with an acceptable current efficiency (about 70%) and energy consumption (about 2.2 kWh/kg of cadmium). Electrolysis at 500 mA is preferable being less time consuming.

Nickel recovered as NiCO_3 is 98% of the nickel present in the electrode powder.

A flow-sheet for the recovery procedure is given in Fig. 6.

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