

Advances in the recovering of spent lithium battery compounds

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Abstract

Advances in a process based on simple and environmentally compatible operations, aimed to the treatment and recycling of spent lithium-ion batteries, are reported in this paper. This process is safe, economic, and recovers as much of the battery materials as possible. It operates mainly in a selective dissolution in dilute acid, a chemical treatment of the filtrate and a thermal treatment of the solid residue. The validity of the process and its reproducibility have been evaluated at each step of the separation. This method involves very simple equipment and can be scaled-up for commercial production. Based on the projected quantities of lithium ion batteries available for recycling in the next few years, there is a significant market opportunity for a successful technology.

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1. Introduction

The growth of energy demand for portable equipments greatly increases batteries consumption and, consequently, increases the produced metal-containing hazardous waste. The storage capacities of special waste dump sites are limited, and the disposal costs are very high. Moreover, the French law regarding collection and elimination or recycling of cells and storage batteries has been reinforced since January 2001 and it must be applied to all the types of batteries. So, recycling of the major components of spent cells appears to be a beneficial way to prevent environmental pollution and raw material consumption, while meeting the new legal requirements [1,2].

Lithium primary cells have been introduced to the market for about 25 years, while lithium secondary batteries— or storage batteries—have less than 10 years of commercial development [3–5]. Extensive research is currently going on to improve the secondary lithium battery technology. Significant improvements consist in new design of electrolyte system (polymer electrolyte) and replacement of the lithium metal negative electrode by lithium-storing materials, typically graphitic carbon, while the positive electrode is a lithium-containing compound like LiCoO_2 , LiMnO_2 , or

related oxides. These new storage batteries are usually referred to as “lithium ion cells”.

Li-containing batteries are extensively used as electrochemical power sources in modern-life equipments: cellular phones, computers, camcorders or in medical implants or accessories like cardiac pacemakers. High-power lithium batteries are devoted to military applications, aerospace and electric vehicles. Due to their high energy density, high cell voltage, long storage life, low self-discharge rate and large temperature range, lithium batteries are often preferred to conventional systems with aqueous electrolytes. The increase of the waste flux generated and the growth of environmental awareness have conducted to the development of programs to recycle spent batteries [6–16]. Most of the proposed processes are based on hydrometallurgy chemistry and are developed at a laboratory scale [7,12–14,16]. Because of high reactivity of lithium in air or moisture, lithium-metal batteries are industrially processed only in a few places (Canada and USA) by Toxco Inc. and BDC Inc. using low-temperature process recycling plants [17]. Lithium-ion batteries are reprocessed in France (SNAM) or in UK (AEA technology batteries) [15] mainly with the aim to recover electrolyte and valuable metals from the positive electrode.

The process proposed in this paper operates through a selective dissolution in dilute acid and selective precipitation of metals as hydroxide compounds from the filtrate; our method decomposes into two steps: at first, the treatment of

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standardized solutions and then the treatment of commercial cells.

2. Experimental

2.1. Materials

The selected material is composed of cylindrical cells (A), button cells (B) and a lot of various cells (C) from different suppliers, as a representative sample of the real waste material.

First, lithium cells from both the A and B samples are opened; the separated parts are submitted to qualitative analysis by scanning electron microscopy associated with EDX probe (JEOL JSM 840 A, 0.2–20 kV). X-ray diffraction analyses were performed on a Siemens D 501 automatic diffractometer using Cu K α radiation source.

In cylindrical cells (A), the anode and the cathode are separated by an insulator film. The cathode is supported on a metal grid. The electrodes and the separator are rolled up together to a spiral wound configuration and inserted in a metallic casing insulated with plastic joints. At the top and the bottom of the cell are the metallic current collectors.

In the “button” models (B), the separator is inserted between the anode and the cathode and stacked as a “sandwich” in a metallic envelope. Insulation of the casing from electrodes is ensured by plastic joints. In some configurations, the cathode is supported on a metal grid.

The metal components of each battery (envelope, cathode, grid) were identified by electron scanning microscopy associated with EDX probe. The EDX diagrams for the different parts of the cells are reported in Figs. 1(A) and 2(B). Lithium, which is the metallic constituent of anode, cannot be detected by the EDX probe analysis. Flame spectrometry has been used to quantify this element. The main identified metals were iron and nickel for the casing, manganese for the cathode. The analyses of Mn²⁺ and Ni²⁺ (or Fe³⁺) ions were carried out by ionic chromatography, after dissolution of the battery in concentrated hydrochloric acid (10 mol l⁻¹). Typical metal compositions for a cylindrical lithium cell (A) and for a button lithium cell (B) are given in Table 1. The metallic part of the batteries is mainly due to the steel casing which nearly represents 50% of the cell mass;

Table 1
Quantitative analysis of metallic part of lithium cells

Elements	Cylindrical cell concentration (wt.% \pm 0.2)	Button cell concentration (wt.% \pm 0.2)
Li	1.5	1.8
Mn	9.6	16.4
Co	0.1	0.1
Fe	34	41.3
Ni	5.4	3.0
Cr	9.6	9.6
Mo	0.8	0.1

the plastic part (external cover, joints, etc.) is evaluated in the range of: 27–40% of the mass.

2.2. Valorization process: selective precipitation

After dissolution of the opened battery in an acid media, the metal part is selectively precipitated in its stable hydroxide form as a function of the pH, according to its solubility product.

To test the separation process, we prepared standardized solutions containing some of the preliminary identified cell metals. Starting from metal nitrates, three standard solutions were prepared (see Table 2), all containing lithium and manganese ions associated with nickel or iron in a similar molar ratio to that existing in batteries.

The metal hydroxides are obtained when sodium hydroxide solution (10 mol l⁻¹) is added to the nitrate solution (200 ml) until the pH conditions of metal hydroxide precipitation are reached [18]. The precipitate is then filtered off. As the hydroxide precipitates are difficult to characterize, they were calcinated at 1000 °C for 2 h to obtain corresponding oxides, easily identified by X-ray diffraction. In the presence of nickel (standardized solution (2)), the solution is firstly treated with dimethylglyoxime to form a red solid complex with the nickel. The complexation reaction is very selective and quantitative. Lithium and manganese are then separated adding sodium hydroxide solution.

The operating conditions and separation results are reported in Table 2.

The selective precipitation separation process was applied on spent Li ion batteries, after preliminary dissolu-

Table 2
Experimental conditions with standardized solutions

S.no.	Metal content of the standardized solution (molar ratio)	Initial pH	NaOH ^a (ml)	Results	
				Filtrate content	Precipitate content
(1)	Li–Mn (0.08–0.1)	3.8	30	Li (100%)	Mn (100%)
(2)	Li–Mn–Ni (0.08–0.1–0.02)	2.9		Li and Mn (100%) for further separation see solution (1)	Ni ^b (100%)
(3)	Li–Mn–Fe (0.08–0.1–0.2)	0.71	16	Li (100%) Mn (90%) for further separation see solution (1)	Fe (100%) Mn (10%)

^a Volume (ml) of NaOH solution (10 mol l⁻¹) added to 200 ml nitrate solution to reach the pH of metal hydroxide precipitation

^b Ni extracted from the solution after complexation with dimethylglyoxime.

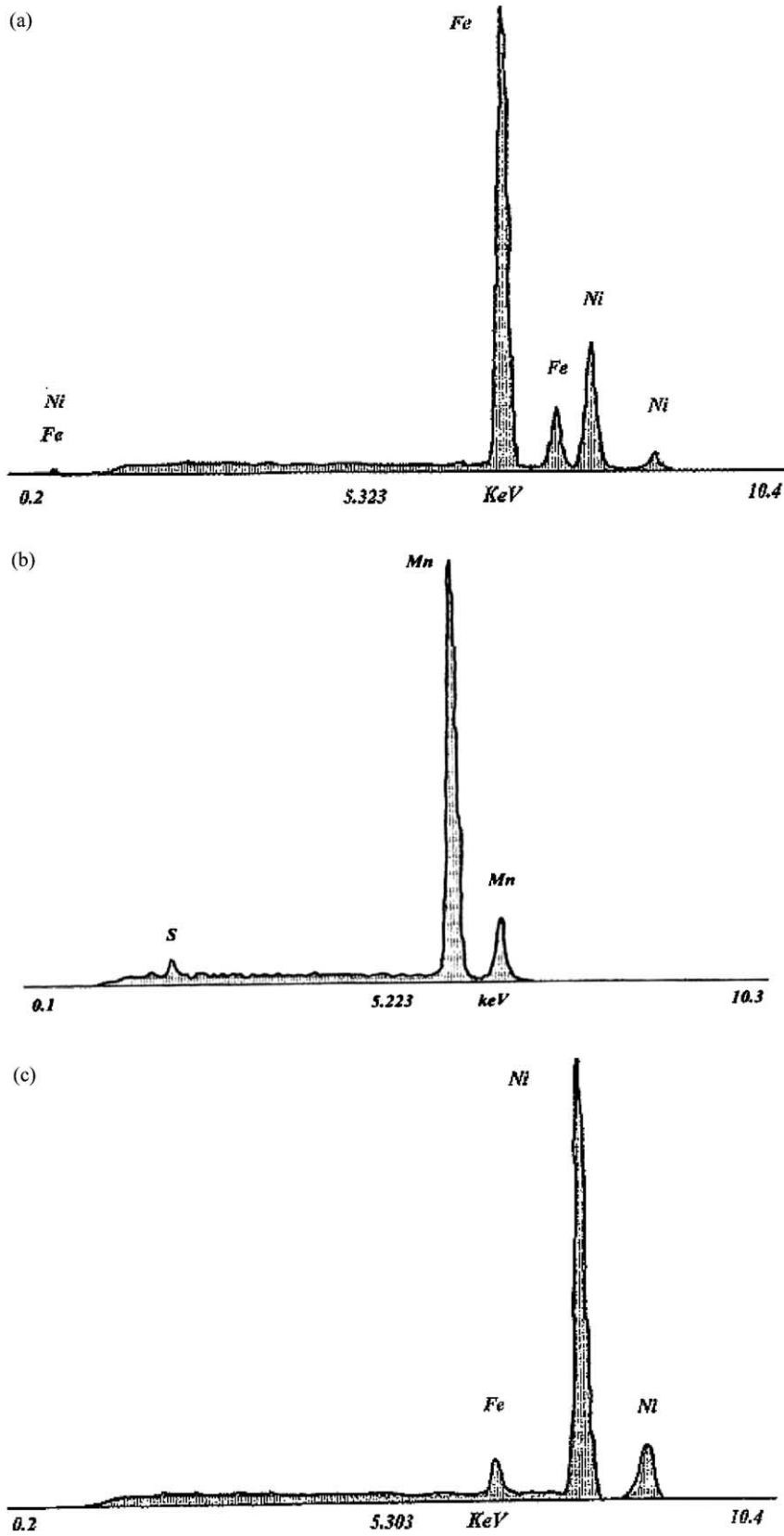


Fig. 1. Cylindrical cell (A) energy diagrams: (a) external envelope (jacket), (b) cathode and (c) grid.

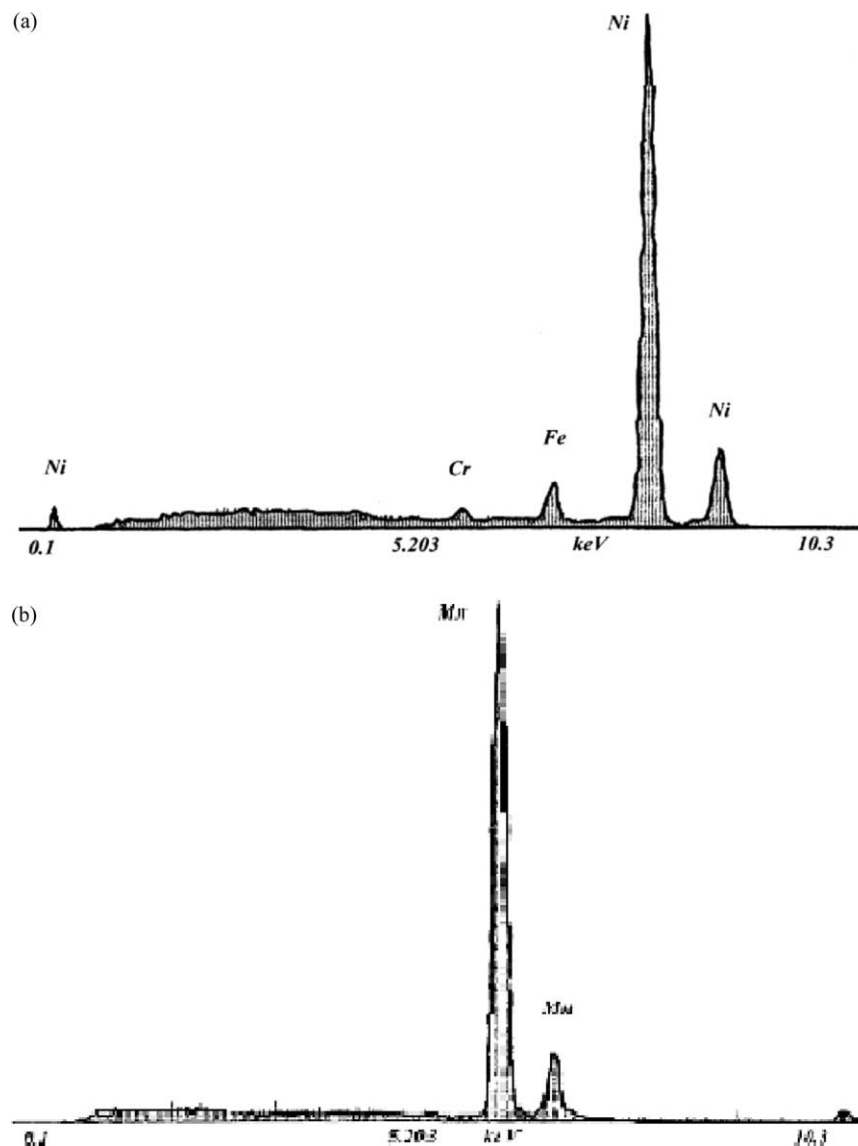


Fig. 2. Button cell (B) energy diagrams: (a) external envelope and (b) cathode.

tion in acidic medium. The choice of the acid is reported hereafter.

3. Results and discussion

We have experimented various separation techniques and retained a treatment in an acidic medium directly followed by a series of metal selective precipitations as a function of pH. This choice of hydrometallurgical treatment does not involve organic solvents, taking into account the environmental aspect.

3.1. Study of a spent standard battery (ref A)

First, a commercial, cylindrical spent battery (ref A) is opened to increase the contact area with solvent and is then

immersed in 200 ml of acid to be partially dissolved. This commercial lithium-ion battery is standardised and its composition is well known (see Section 2). The main aim is to recover a maximal quantity of lithium and of transition metals upon the first step. It is obvious that this stage strongly depends on the dissolution agent and acid concentration. The influence of both nitric and hydrochloric acids has been studied. The acid concentration varies in the range of 0.1–5 mol l⁻¹. Baths are thermostated at 80 °C and are magnetically stirred. Various samples are taken away at several dissolution times (between 0 and 6 h). These experiments are carried out in order to determine the dissolution profiles and the selectivity of the method.

Dissolution in hydrochloric acid, even for very small concentrations (typically 0.1 mol l⁻¹), only leads to a lithium recovering of 80% after 2 h (Fig. 3) with a significant quantity of dissolved manganese (already 25% after 1 h).

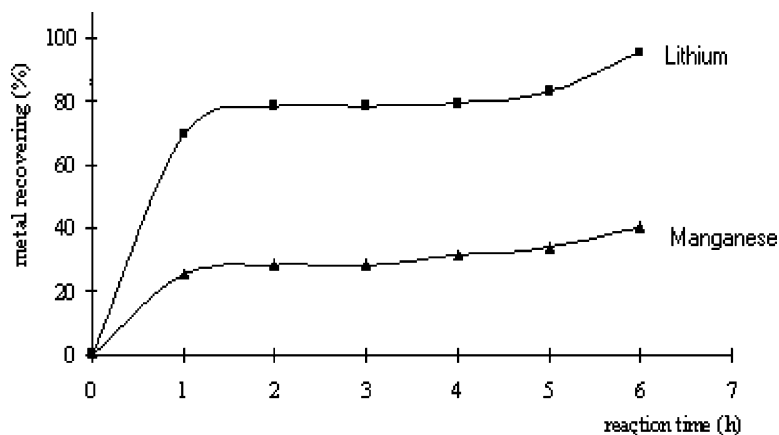


Fig. 3. Metals recovery (%) vs. dissolution time in hydrochloric acid.

To prevent manganese dissolution, the HCl concentration is to be reduced but involves a too long dissolution time, not suitable for an industrial process.

So, we have carried out tests with nitric acid under the same conditions but concentration varying from 0.5 to 5 mol l⁻¹. The spectrophotometric analyses results show that when the concentration is ranging between 1 and 2 mol l⁻¹, we approximately recover 100% lithium (Fig. 4). In the same time, samples have been analyzed at different times by ionic chromatography to quantify manganese. Results prove that manganese is even present for very dilute acid (Fig. 5). On the other hand, the filtrate does not contain other ions than Fe³⁺, Ni²⁺ and Co²⁺ if the nitric acid concentration does not reach 5 mol l⁻¹.

In this study, we have made the choice, during the first stage, to separate the whole content of lithium and manganese from other metals with a nitric acid concentration of 2 mol l⁻¹. We have then performed a separation method between lithium and manganese in the filtrate. To begin with, an increase of the solution pH to 5.2 makes the precipitation of few still present nickel and iron traces possible. This second filtration guarantees the composition of the

filtrate (exclusively constituted by lithium and manganese). An addition of NaOH solution to reach pH = 10 allows the selective precipitation of manganese hydroxides. Then, we can notice a very good reproducibility of the separation method. Fig. 6 shows the process flow-sheet designed in this work.

3.2. Study of a batteries mixture (ref C)

A representative sample (ref C) of the “material” heterogeneity to treat is prepared by mixing fifteen spent batteries of different mark and composition. They are opened like previously but during the cutting we noticed a strong heating, caused by the internal short-circuit of the cell. On a large scale, refrigeration during this operation is strongly advisable (with liquid nitrogen for instance), in order to prevent safety hazard due to flames and explosions.

The opened cells were submitted to the previous treatment protocol as indicated in Fig. 7. After the first filtration, we recover 100% lithium and 95% manganese in the filtrate. The precipitation of the manganese hydroxides at pH = 10 with addition of a NaOH solution then makes possible a

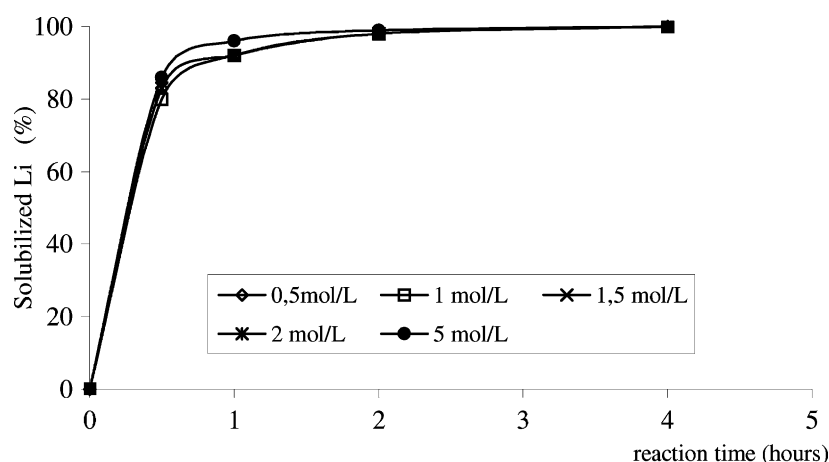


Fig. 4. Lithium recovery (%) vs. dissolution time in nitric acid at various concentrations.

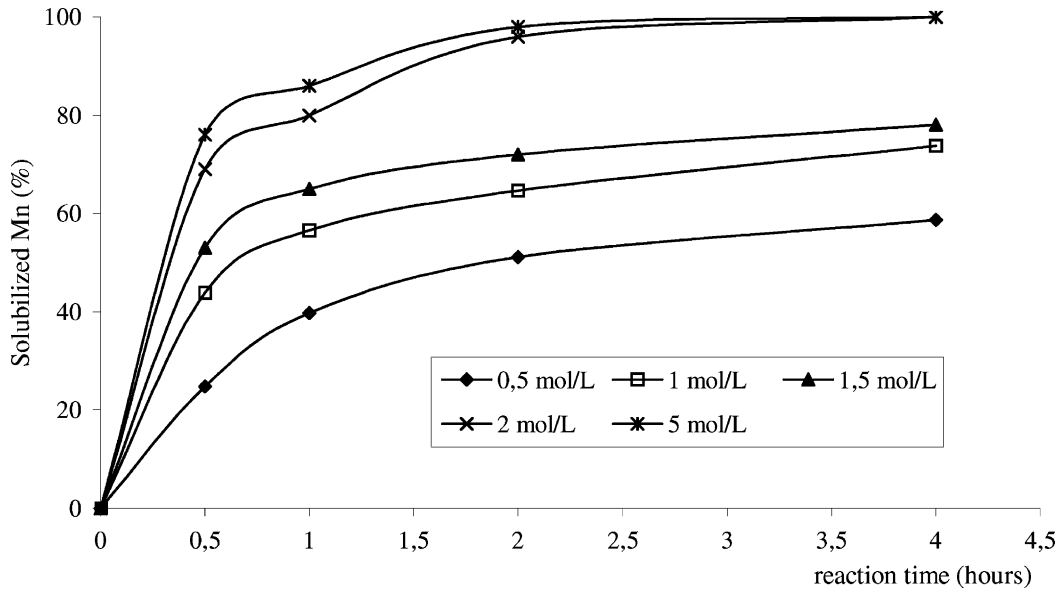


Fig. 5. Manganese recovery (%) vs. dissolution time in nitric acid at various concentrations.

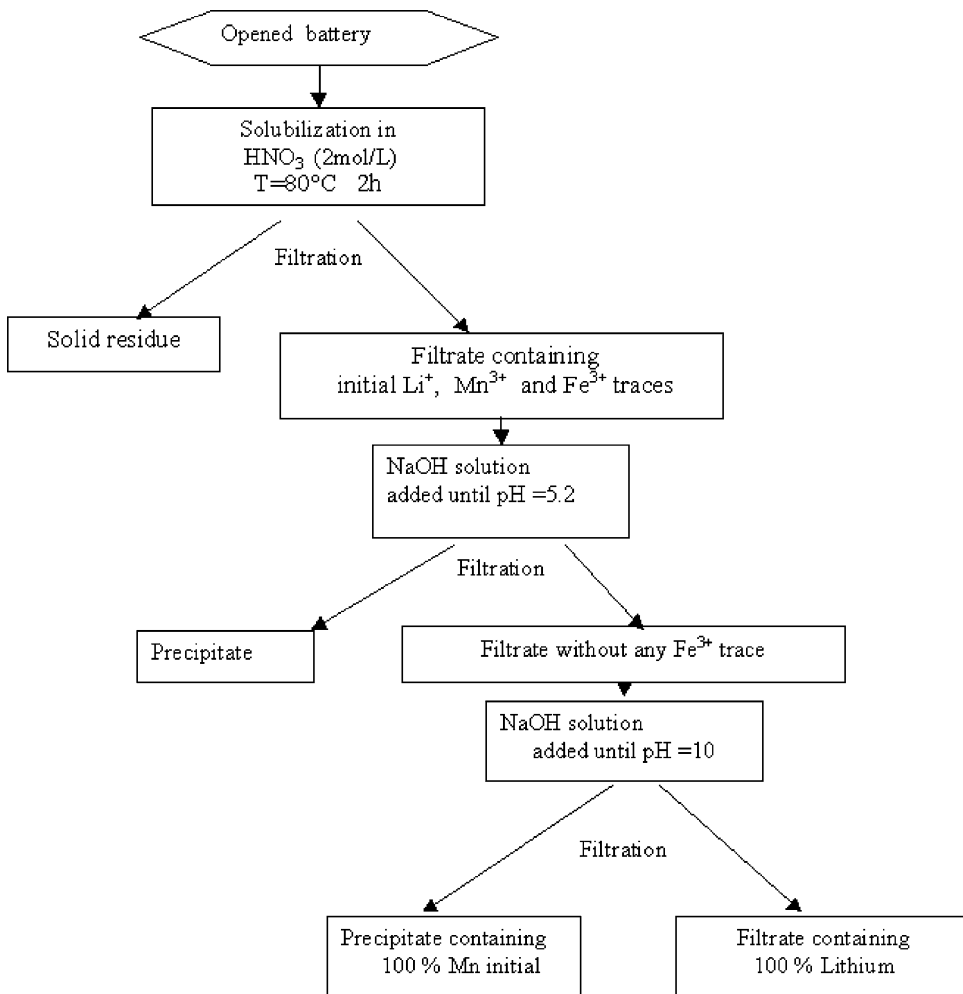


Fig. 6. Flow-sheet of the recycling process for battery (ref A).

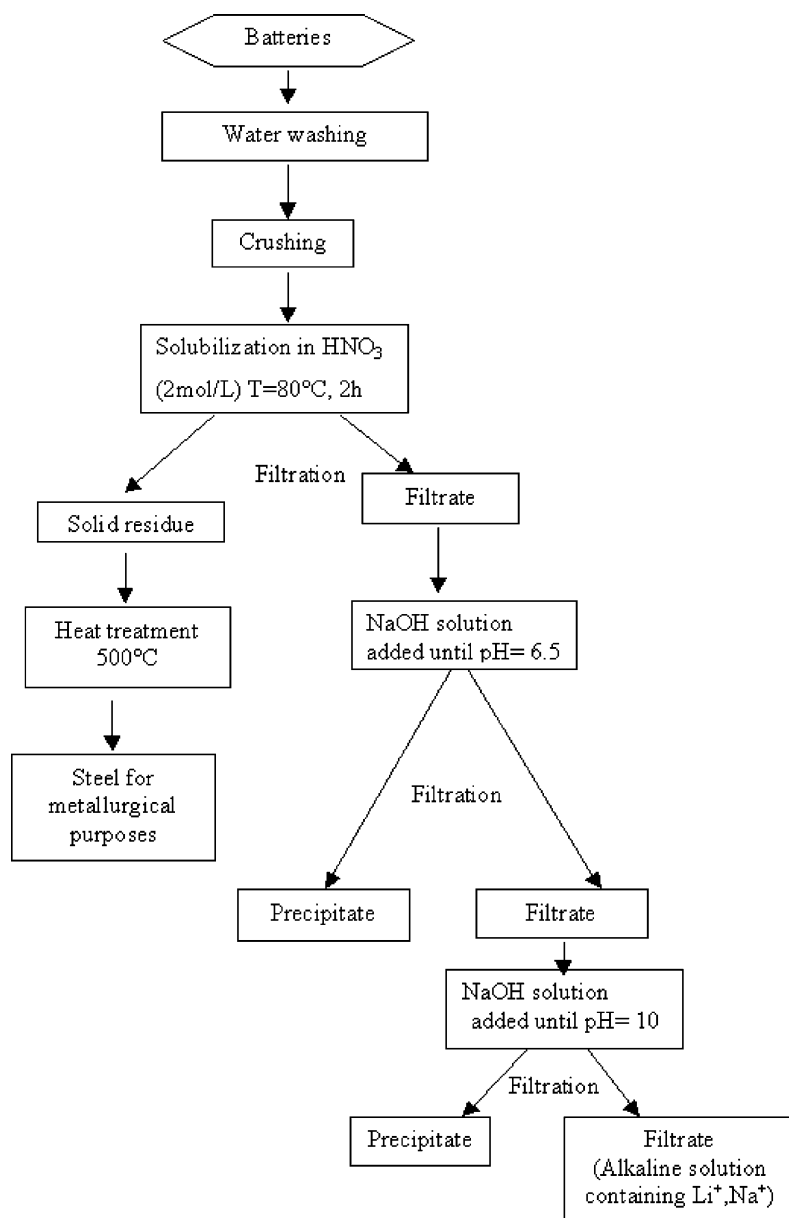


Fig. 7. Flow-sheet of the global recycling process.

good separation between lithium and manganese. NaOH, which is a strong base, allows to work with small solution volumes. On an industrial scale, this step can be controlled by using an adequate pH sensor. So, $\text{Mn}(\text{OH})_3$ precipitate can be easily separated from the solution by filtration. The alkaline ions, Na^+ , coming from NaOH are recovered, at the last step, mixed with the alkaline ions, Li^+ . The solid residue (Fig. 7) consisted of a iron, cobalt and nickel hydroxides mixture and some traces of $\text{Mn}(\text{OH})_3$ is introduced into a muffle furnace at 500°C during 2 h to eliminate carbon and organic compounds. The alloy can then directly undergo beneficiation in metallurgical applications. Furthermore, it is also possible to consider a thermal valorization by recovery of combustion gases of organic and plastic compounds at the calcination furnace output.

4. Conclusion

Spent batteries and especially spent lithium batteries are explicitly mentioned on regulations of waste management. For few years, recycling processes begin to appear in some countries, but improvement in this field is still to be done taking into account safe and environmentally compatible operations. There are two major problems with the development of an efficient valorization process: the heterogeneity of the waste and the non-reproducibility of the material to treat. It is, thus, necessary to consider a very rigorous sorting what appears not easily feasible in the near future. Another possibility is the development of very flexible industrial processes. Our work is located in this second framework.

Our aim was to recover all the valuables contained in the waste, in the form of compounds ready to be used in industrial applications.

We have tackled the problem by two different ways. First, we have studied standardized solutions (typically Li–Co–Mn) constituted by a mixture of alkaline and transition metals of a well-known composition, in order to define the selective precipitations. Then, on the basis of the achieved results, we considered the chemical treatment of a batch of spent lithium batteries consisting in a representative mixture of commercial cells. Consequently, we propose a process which allows to achieve a good recovery of the battery components and to separate the “metal families” (alkaline metals, pure manganese oxides, metallurgical alloy (Fe, Cr, Ni, Co)) and even combustion gases for an energetic valorization. Characterizations of the recovered metals were performed by quantitative means available in the laboratory (ionic chromatography, atomic absorption spectroscopy).

The valorization process proposes to recover the insoluble plastics, the transition metals, a solution of alkaline ions (Na^+ and Li^+) and a metallurgical alloy which may undergo beneficiation. Improvements would be made in order to achieve a complete separation of the metals.

According to the projected numbers of cells available for recycling, and the value of a cell content, there is a significant market opportunity for recycling lithium ion cells and batteries.

The economic and environmental interests related to the valorization of this type of waste are really significant, which justifies search and improvements in this field.

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