Short communication

# Recovery of valuable elements from spent Li-batteries

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## Abstract

This work examines two recycling processes for spent $Li/MnO_2$ and Li-ion batteries. The anode, cathode and electrolyte ($LiPF_6$) were submitted to one of the following procedures: (a) calcination at 500 °C (5 h) followed by solvent extraction to recover lithium salts (fluoride, phosphate) in good yield (90 wt%). The residual solid was treated with $H_2SO_4$ containing $H_2O_2$ and on evaporation gave high purity grade cobalt or manganese sulfate; (b) fusion with $KHSO_4$ (500 °C, 5 h). The resulting aqueous solution was added dropwise to a solution of NaOH, giving cobalt or manganese as impure precipitate. Addition of KF precipitated high purity grade LiF in moderate yield (50 wt%). The final aqueous solution on treatment with calcium sulfate precipitated the corresponding phosphate and fluoride salts.
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*Keywords:* Li-ion batteries; $Li/MnO_2$ batteries; Metals recovery

## 1. Introduction

For environmental and efficiency reasons, lithium batteries have been a preferred portable source energy for small electronic devices [1], and tend to replace Ni–Cd and Ni–MH (nickel metal–hydride) batteries. There are two basic lithium batteries: $Li/MnO_2$ and lithium-ion systems.

At present the $Li/MnO_2$ battery is mainly used in digital cameras [2,3]. Since lithium is very reactive towards water, these batteries employ a non-aqueous solvent in a sealed container. The lithium-ion battery was proposed as a new portable energy source in 1990 [2,4]. It employs $Li^+$ ions which are present in the electrolyte as soluble salts in non-aqueous solvents: in the cathode as $LiCoO_2$, and in the anode as lithium carbide ($LiC_y$). During discharge lithium ions go from the anode to the cathode. The lithium-ion battery [2,3,5,6] presents a high energy density, long life cycles, very low self-discharge and safe handling. The battery employs low-density materials, presenting low mass and size. The distance between the two poles is usually 50 μm (0.05 mm). A polymer foil (polyamide or polypropylene) is placed between the cathode and the anode in order to avoid electrical contact.

A significant increase of the lithium battery market is underway, as judged from the 1998–2003 period (growth from 8.4% to 28% of the portable energy market in the developed world [7,8]). The world lithium-ion battery consumption reached 700 million units in 2004 [9] (500 million in 2000 [7] and 250 million in 1998 [10]). The consequence of this expansion will be an increased requirement to dispose of spent batteries in the forthcoming years [2–4,8,11] (the battery lifetime is usually 2 years [8]). In general, spent lithium batteries are discarded in the domestic waste [3,12], which is environmentally unacceptable. Therefore, it is necessary to define clearly in environmental directories what should be the correct final destination [11]. It is estimated that the amount of spent lithium-ion batteries may reach 200–500 ton/year (2002–2006), with significant amounts of cobalt (5–20 wt%) and lithium (2–7 wt%) [7,10].

The great environmental advantage of the lithium batteries is the absence of dangerous heavy metals, such as mercury, cadmium and lead [11–13]. However, after corrosion of the external steel case, the toxic and flammable non-aqueous solvent is put in contact with the environment. The residual lithium metal of the $Li/MnO_2$ battery reacts vigorously with water, thus producing heat and flammable gas ($H_2$) [1,11,13,14]. These features make both final destination and recycling processes of spent lithium batteries dangerous, since there is risk of fire and ignition. An attempt to disassembly a battery without security measures may expose the product to moisture, causing violent

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reactions, short-circuit and ignition of the non-aqueous solvent [3].

Processing of spent lithium batteries is relatively simple because the chemistry of their components is very different and there are relatively few elements present [4,8,11,15]. They have been recognized as a secondary source for Li, Co and Mn [16,17]. It is necessary to take into account the presence of some elements in minor amounts, which can make recycling difficult because of chemical interference. It is very difficult to recover the electrolyte (usually $LiPF_6$, of high cost) because it is very reactive [11] towards water, moisture and heating. Recovery by solvent extraction at low temperature has been tested [11].

The laboratory recycling processes found in the literature employ leaching with dilute HCl [2,3], $HNO_3$ [7,10] or $H_2SO_4$ [4,9,17,18], followed by treatment of the acid leachate and management of the final wastes. $H_2O_2$ is usually added [7,9,10,18] in order to convert all cobalt or manganese to the +2 state for subsequent recovery by electrochemical [9], precipitation [7,10] or solvent extraction [2] techniques. It is possible to recover lithium together with cobalt as $LiCoO_2$ mixed oxide (the basic cathode component) [10] or alone, as carbonate ($Li_2CO_3$) [4,16,17] at 100 °C, presenting the lowest solubility in water [19]. Carbon is usually recovered as insoluble matter after the leaching process [3,4].

This work aimed at developing new hydrometallurgical processes applicable to both $Li/MnO_2$ and Li-ion batteries, with emphasis on recovery of the metals present and generation of low amounts of final wastes.

## 2. Experimental

### 2.1. Raw materials

Twenty lithium-ion and thirty $Li/MnO_2$ batteries (manufactured between 2000 and 2004) were employed in this study.

Their residual voltage was measured with a digital multimeter. All samples were stored at −5 °C and manually disassembled in a fume-hood. After removal of the steel case they were left to stand for 1 h in a vacuum system. During this period the temperature of the $Li/MnO_2$ battery raised from 25 to 45 °C. Vacuum was applied for 20 min to recover the solvent. The sample without solvent was fully disassembled by mechanical vibration and manual removal, allowing recognition and separation of the components (cathode, anode, plastic case, steel case, copper foil, aluminum foil, polymer foil and electrical contacts). Masses were determined in an analytical balance.

### 2.2. Fusion with KHSO₄

The "active mass" (cathode + anode + electrolyte) was mixed with $KHSO_4$ at a 1:8–9 sample/flux mass ratio. The mixture in a crucible was placed in a furnace at 500 °C for 5 h in air in order to avoid any reduction of sulfate to $SO_2$ and/or sulfide species by the carbon present. The roasted mass was cooled down in the furnace and leached with distilled water at 90 °C for 1 h under stirring (300 rpm). The pink ($Mn^{2+}$) or red ($Co^{2+}$) solution was added slowly to NaOH (6 mol L$^{-1}$) keeping the pH above 9. When manganese was present, $H_2O_2$ (30 wt%) was added in order to oxidize it to the +4 state. The crude precipitate containing cobalt or manganese was filtered and washed with water (6 mL g$^{-1}$ solid). A saturated KF solution was added dropwise to the filtrate, giving a translucid-white precipitate (LiF), which was filtered and washed with HF (0.01 mol L$^{-1}$) and water (5–10 °C). The final effluent was treated with $CaSO_4$ (saturated solution) in order to precipitate soluble phosphate and fluoride ions present and neutralized with $H_2SO_4$ (1 mol L$^{-1}$). The process scheme is shown in Fig. 1. The experiments were run in triplicate, and errors for each experiment were always below 3%. In separate experiments the "active
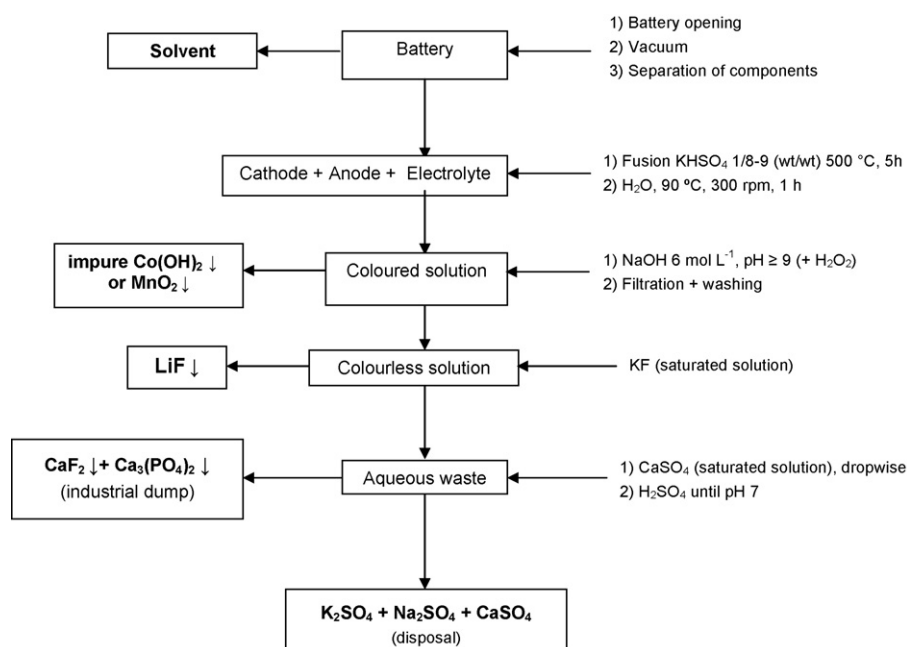


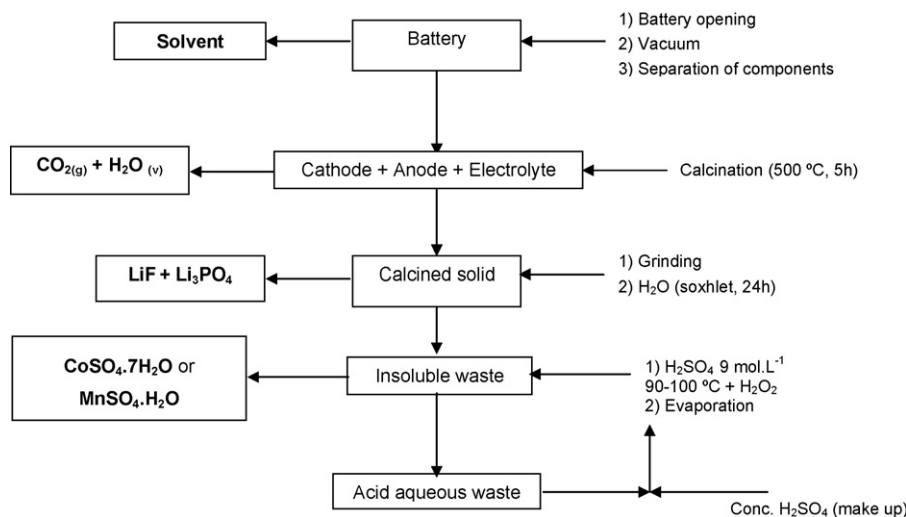Fig. 1. Scheme for processing spent lithium batteries by fusion with $KHSO_4$.

Fig. 2. Scheme for processing spent lithium batteries by previous calcination.

mass" of the lithium-ion battery was processed together with the metal and polymer foils under the same experimental conditions.

### 2.3. Previous calcination

The "active mass" was calcined in a furnace at 500 °C (5 °C min$^{-1}$) for 5 h. Carbon was eliminated in this way. The calcined solid was placed in a Soxhlet apparatus in order to recover lithium salts by extraction with water (24 h). The aqueous solution, which presented a milky aspect, was evaporated, giving a white mass. The extracted solid was treated with $H_2SO_4$ (9 mol L$^{-1}$) at 90–100 °C (3 mL g$^{-1}$ solid), with addition of $H_2O_2$ (30 wt%) to reduce all cobalt or manganese to the +2 oxidation state. After about 2 h, the solid was dissolved and the solution was evaporated. After 2 h, brilliant red (CoSO$_4$·7H$_2$O) or pale pink (MnSO$_4$·H$_2$O) crystals were obtained, isolated by filtration, washed with ethanol and dried at room temperature. Two different processes were applied to the residual acid solution: (a) neutralization with NaOH, followed by filtration and washing of the precipitate with water (8 mL g$^{-1}$ solid); (b) reuse for treatment of new samples of extracted solids. In this case, sulfuric acid was added to compensate losses after crystallization of manganese/cobalt sulfates. The process scheme is shown in Fig. 2. The experiments were run in triplicate, and errors for each experiment were always below 2%. In separate experiments the "active mass" of the lithium-ion battery was processed together with the metal and polymer foils under the same experimental conditions.

### 2.4. Analytical methods

X-ray diffraction (XRD) analysis was accomplished using Cu Kα as radiation source. Calibration curves for X-ray fluorescence analysis (XRF) were made using Co, Mn, Cu, Fe and Li standard solutions (0.1–1.0 g L$^{-1}$). Carbon content was determined by LECO analyzer. Lithium salts were analyzed by ion chromatography and qualitative tests [19].

Table 1
Residual voltage of the spent Li/MnO$_2$ batteries used in this study

| Voltage (V) | Amount |
| --- | --- |
| 0.0–0.5 | 4 (13.3%) |
| 0.5–1.0 | 1 (3.3%) |
| 1.0–1.5 | 1 (3.3%) |
| 1.5–2.0 | 2 (6.7%) |
| Above 2.0 | 22 (73.4%) |

## 3. Results and discussion

### 3.1. Residual voltage of Li/MnO$_2$ batteries

The lithium-ion batteries presented no residual charge. On the other hand, data in Table 1 show most Li/MnO$_2$ batteries present a considerable residual voltage, which means the presence of non-reacted lithium. This result has already been described in the literature [4], and emphasizes the need for full discharge of the battery before disposal or recycling [7].

### 3.2. Composition of Li/MnO$_2$ batteries

The average weight composition is shown in Table 2. The cathode and the anode together correspond to 70 wt% of the overall battery. It was not possible to quantify the electrolyte itself because it was dispersed between the cathode and the

Table 2
Average composition of the Li/MnO$_2$ batteries

| Component | Amount (wt%) |
| --- | --- |
| Cathode (MnO$_2$ + C)[a] + electrolyte | 70.0 ± 0.9 |
| Nickel grid | 12.9 ± 0.2 |
| Polymer foil (cathode–anode separator) + electrolyte | 7.1 ± 0.3 |
| Steel case | 5.2 ± 0.4 |
| Non-aqueous solvent | 4.8 ± 0.5 |

[a] Carbon corresponds to 15–17 wt% of the cathode (11–12 wt% of the overall sample).

Table 3
Average composition of the lithium-ion batteries

| Component | Amount (wt%) |
|---|---|
| Cathode + anode + electrolyte[a] | 39.1 ± 1.1 |
| Plastic case | 22.9 ± 0.7 |
| Steel case | 10.5 ± 1.1 |
| Copper foil | 8.9 ± 0.3 |
| Aluminum foil | 6.1 ± 0.6 |
| Polymer foil (cathode–anode separator) + electrolyte | 5.2 ± 0.4 |
| Non-aqueous solvent | 4.7 ± 0.2 |
| Electrical contacts | 2.0 ± 0.5 |

[a] Carbon corresponds to 30–32 wt% of these components (12–13 wt% of the overall sample).

anode. The steel case corresponds to a much smaller amount than found in ordinary alkaline and Zn/C batteries (45–50 wt%) [20], as the internal medium is not corrosive. The non-aqueous solvent found was propylene carbonate (90% of samples) and 1,3-dioxolane (10%), in agreement with previous literature data [4,21].

Analysis of the "active mass" by X-ray fluorescence (XRF) showed the presence of manganese and lithium as the main metals present. Sodium, iron and calcium were found in small amounts. XRF and atomic absorption data indicate the following amounts (wt%, whole battery): Mn: $32.0 \pm 2.5$; Li: $8.5 \pm 0.6$; Fe: $0.3 \pm 0.1$. Only phosphorus peaks were found in XRF spectra, suggesting the presence of $LiPF_6$ as the electrolyte in all samples, in agreement with other studies [1,14,15].

### 3.3. Composition of lithium-ion batteries

The composition of this battery is more complex than that of $Li/MnO_2$ (Table 3). The "active mass" corresponds to almost 40 wt% of the overall weight. XRF showed the presence of cobalt, lithium and copper as the main metals present, with minor amounts of aluminum, calcium and chromium. Phosphorus peaks were identified, confirming the use of $LiPF_6$ as the electrolyte in all samples [22]. The steel case is much thinner than found in alkaline and Zn/C batteries [20], as the internal medium is not corrosive. The non-aqueous solvents found were propylene carbonate (75%), 1,3-dioxolane (20%) and dimethoxyethane (5% of samples). It is essential to eliminate the solvent completely because the presence of even residual amounts makes cathode isolation from the copper foil and anode from the aluminum foil very difficult, with risk of disintegrating such foils, contaminating the "active mass".

### 3.4. Lithium recovery

Direct recovery of lithium by extraction with water gave very low yields (less than 20 wt%) because of the presence of a strong absorbent medium (carbon). The strategy adopted in this work was a previous calcination to eliminate this element. Loss of volatiles corresponded to 13 wt% of the lithium-ion battery, in agreement with the value given in the literature [16 wt% – 7,19]. Carbon content reached 15 wt% of the $Li/MnO_2$ battery (16 wt% by LECO analyzer). Calcination greatly improved lithium salts
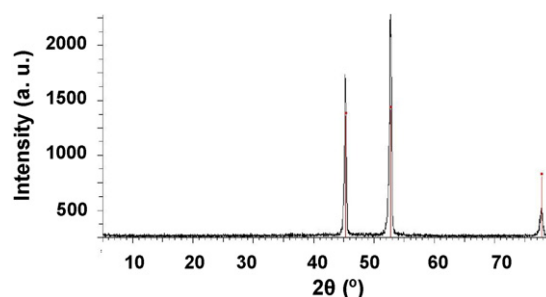


Fig. 3. X-ray diffractogram of the LiF precipitated with KF.

recovery (ca. 90 wt%). This result is in contrast to the low reactivity of the calcined solid described in the literature [17]. This may be explained by the low heating rate applied in this work ($5\,°C\,min^{-1}$), avoiding ignition of the carbon, with formation of mixed oxides and other refractory compounds.

According to qualitative tests [19], lithium is present as two salts, LiF and $Li_3PO_4$, which are sparingly soluble in water [19]. Ion chromatographic analysis indicates that LiF corresponds to 70–80 wt% of the solid. The recovery of lithium from such salts is higher than recovery as carbonate (around 70–80 wt%) [4,16]. Both lithium salts present commercial value [23], but it is necessary to treat the mixture in order to recover a single final product.

In the fusion route, lithium is recovered only after cobalt or manganese and the yield is lower. However, lithium can be obtained as a single compound (LiF) with a purity over 99 wt% (ion chromatographic analysis). XRD results presented in Fig. 3 show that this salt is well crystallized. LiF cannot be precipitated before cobalt/manganese because $MnF_2$ and $CoF_2$ are not very soluble in water [19]: they tend to co-precipitate with LiF.

### 3.5. Recovery of cobalt and manganese

In the calcination route, after extraction of lithium salts with water, the solid presented a dark-grey colour. XRD showed the presence of a lithium-manganese mixed oxide (Fig. 4) or a lithium-cobalt mixed oxide (Fig. 5). These species could explain the non-quantitative lithium recovery by water extraction. Taking into account the presence of copper (or iron) and non-extracted lithium, the treatment of this solid with $H_2SO_4$ aimed at obtaining a high purity final cobalt/manganese product. Solubilization was a slow process. Direct treatment of the
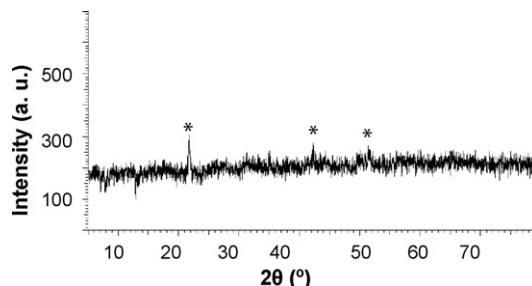


Fig. 4. X-ray diffractogram of the Li–Mn oxide ($Li_4Mn_5O_{12}$) obtained on extraction of the calcined solid with water.
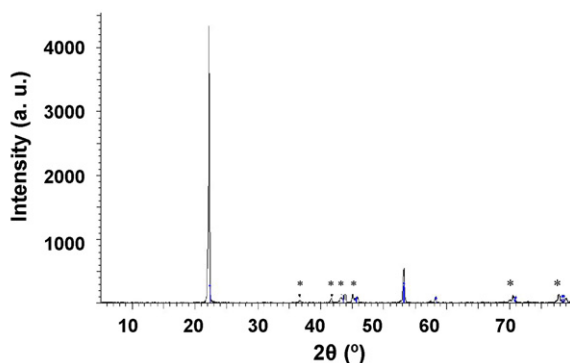
Fig. 5. X-ray diffractogram of the $LiCoO_2$ oxide obtained on extraction of the calcined solid with water. Peaks assigned "*" correspond to $Co_3O_4$.

original (non-calcined) solid with $H_2SO_4$ under the same experimental conditions was faster (60–80 min), but separation of carbon proved a very difficult task. It required much more water during washing (15 mL g$^{-1}$), thus diluting the final acid solution and increasing energy consumption in the evaporation step (Fig. 2). Carbon isolated in this way corresponds to 12 wt% of the lithium-ion battery. This result is in agreement with previous data obtained after direct calcination (13 wt% of the original solid), by the LECO analyzer (12 wt%) and literature data [7,18]. Carbon isolated form the Li/MnO$_2$ battery corresponds to 17 wt% of the original sample. This result is close to the value obtained after previous calcination (15 wt%) and by the LECO analyzer (16 wt%).

The $MnSO_4H_2O$ and $CoSO_4·7H_2O$ salts obtained presented high purity (over 99.5 wt%). Copper, iron and lithium were not detected under the analytical conditions employed. Manganese and cobalt recoveries were $92 ± 2$ and $94 ± 1$ wt%, respectively.

Chemical analyses of the final acid solution indicate that about 6 wt% of cobalt or 8 wt% of manganese are present, as well as almost all iron or copper and around 10 wt% of lithium. Neutralization with NaOH required much reactant and generated a saturated sodium sulfate solution. After washing the precipitate with water a brown solid was obtained, corresponding to manganese dioxide (together with copper hydroxide and phosphorous) or cobalt hydroxide (containing iron hydroxide and phosphorous). The solution was colourless.

The results obtained after recycling three times the residual acid solution were encouraging: the crystallized sulfate presented the same purity grade and the metal recovery was essentially the same (92–94 wt%). Copper or iron tended to increase concentration in the residual acid solution. A strategy to avoid contamination of the crystallized sulfate is to remove copper or iron from this solution by solvent extraction [24–27].

Cobalt or manganese recovery reached over 99 wt% in the fusion route. Iron and phosphate ions correspond to less than 0.8 wt% of the $MnO_2$ precipitate, and a further purification step may be necessary depending on the intended use. On the other hand, copper corresponds to 3 wt% of the solid containing cobalt. This result requires an additional step to obtain pure cobalt. The crude $Co(OH)_2$ was dissolved in HCl (pH ∼ 2) and 3 mol L$^{-1}$ thioacetamide (90 °C, 200 rpm) was added dropwise, precipitating copper as CuS. Cobalt was reprecipitated as

hydroxide. Precipitation of CuS in acid medium proved a simple way to separate it from cobalt in high yield (>99.5 wt%) and high purity (>99.5 wt% in each final product). The calcium salts (fluoride, phosphate) precipitated from the final aqueous waste (Fig. 1) correspond to less than 2 wt% of the original battery mass.

### 3.6. Effect of addition of copper, aluminum and polymer foils (lithium-ion battery)

The polymer foil was fully destroyed under fusion or calcination procedures. Inclusion of the above components implied introduction of aluminum and copper in the solid to be treated.

Recovery of lithium was drastically reduced (35 wt%) in the previous calcination route (the original result without addition of metal foils was 90 wt%). Formation of mixed oxides and occlusion of lithium salts may account for this result. When the acidic solution was evaporated, recovery of cobalt sulfate (purity 99.5 wt%) reached 60 wt%, 2/3 of the original amount (94 wt%). Aluminum and copper sulfates tended to co-crystallize much earlier than in the process where the foils were not included.

In the fusion route, recoveries of cobalt and copper in the absence or presence of metal foils were similar. However, lithium recovery was affected by the presence of aluminum. When KF was added, $Na_3AlF_6$ and $K_3AlF_6$ salts precipitated, which are more insoluble in water than $Li_3AlF_6$ and LiF [19,24]. The best way to overcome this problem was to precipitate aluminum together with cobalt and copper by adjusting the pH to 8 instead of 10. Lithium can be isolated as fluoride (Fig. 2), with the same yield as in the absence of aluminum. The precipitate can be dissolved in HCl and copper isolated as sulfide (see above). The solution can then be treated with NaOH (pH above 10) in order to precipitate cobalt. Aluminum can be recovered after adjusting pH to 8 with $H_2SO_4$.

Addition of battery components to the processes described in this work made separation procedures more difficult as described. This illustrates the challenge to treat multicomponent samples, such as spent batteries. The tendency on a commercial scale is to grind the battery, and separate some components by physical methods (magnetic, density, etc.). Previous segregation of battery components would also be very profitable for recycling. The plastic case, the polymer foil, the solvent, the steel case, the electric contacts, the aluminum and copper foils are directly recyclable after separation. They correspond to 60 wt% of the spent battery. Separation of the metal foils would also reduce consumption of acids after preliminary calcination or fusion. An alternative to manual isolation of metal foils (impractical on a large scale) or even the use of mechanical processes is to wash the foils with water, followed by recovery of the "active mass" by filtration [28].

### 3.7. Comparison between the two processing routes

Table 4 shows the outline of the two recycling processes described in this work. Phosphate ions contaminate the lithium final product in the previous calcination route or the

Table 4
Comparison between the two routes for processing spent lithium batteries

| Parameter | Route 1 – fusion | Route 2 – previous calcinations |
|---|---|---|
| Solvent recovery | Quantitative | Quantitative |
| Li recovery | 50 wt% (LiF > 99 wt%) | 90 wt%. Mixture of two compounds |
| Co recovery | >99 wt%. Presence of copper and $PO_4{}^{3-}$. Further copper separation step needed | ~94 wt%. High purity grade. Copper and phosphate absent |
| Mn recovery | >99 wt%. Presence of Fe(III) and $PO_4{}^{3-}$ | ~92 wt%. High purity grade. Iron and $PO_4{}^{3-}$ absent |
| Waste generation | High | Low (recycling of the acid liquor) |
| Energy consumption | Lower (fusion, dissolution in water and copper precipitation as CuS) | Higher (calcination, Soxhlet extraction, solubilization of the Co/Mn solid and evaporation of the sulfuric medium) |

cobalt/manganese precipitate obtained, in the fusion route. The allowed amount of phosphorus in these final products will determine the need of a supplementary purification step.

The importance of recycling is very clear in the calcination route, since it reduces the amount of final wastes and consumption of reactants, water and energy. Recycling is not possible in the fusion route: the excess of flux and the precipitation of manganese/cobalt generating high amounts of final wastes. This situation is reversed when energy consumption is discussed: the fusion route is energetically more economical. The cost of water, energy, reactants and disposal of the final wastes will determine the final choice.

## 4. Conclusions

Both processing flowsheets reported for spent lithium batteries present the following merits: (i) higher recovery of cobalt, manganese and lithium than in most studies in the literature; (ii) partial recovery of electrolyte components that are usually lost in conventional processes; (iii) possibility of reduction of final wastes when compared to the classical selective precipitation techniques through reuse of the residual acid solution after cobalt/manganese crystallization. Previous separation of the battery components allowed selective processing of the "active mass" (cathode + anode + electrolyte), thus saving chemicals and energy with respect to the processing of the full battery.

## Acknowledgements

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