

RECOVERY OF LITHIUM FROM WASTE MATERIALS

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In this study, processes based on roasting-leaching-crystallization steps and condensation-precipitation steps for Li_2CO_3 separation from spent Li/MnO_2 batteries and lithium-containing wastewaters were developed and verified on a laboratory scale. Spent Li/MnO_2 batteries were roasted under reduced pressure at 650°C , which split the castings and deactivated the batteries by reduction of LiMnO_2 and MnO_2 with residual lithium metal and graphite to form MnO and Li_2CO_3 . The resultant lithium carbonate was selectively solubilised in water with manganese remaining in the leach residue. Li_2CO_3 of 99.5 % purity was obtained after evaporation of 95 % water. Processing of lithium-containing alkaline wastewaters from the production of liquid rubber comprises condensation up to lithium concentration of 12-13 g/l Li and a two-step precipitation of lithium carbonate using CO_2 as a precipitation agent. Sparingly soluble Li_2CO_3 was produced in the second step at 95°C , whilst most impurities remain in the solution. Obtained lithium carbonate products contained on average more than 99.5 % Li_2CO_3 . The lithium precipitation efficiency was about 90 %.

INTRODUCTION

Lithium carbonate is the most important compound of Li. It is used in various industries, i.e. glass and ceramic. Its advantage lies in forming low-melting fluxes with silica and other materials. Lithium carbonate is also a base for a production of variety of lithium compounds and the Li metal. In the glass and ceramic industry, lithium carbonate is used for production of glass and ceramics having exceptional resistance to thermal shock and practically zero thermal expansivity. For example, glass containing Li_2CO_3 is used for the production of ovenware. Low-fire as well as high-fire ceramic glaze contain Li carbonate as a common ingredient. Its alkaline character provides a contribution to changing the state of metal oxide colorants in glaze, especially Fe_2O_3 . It also causes more rapid setting of cements. Lithium carbonate is used for a production of variety of special materials as well. Manufacturing of low-temperature sintering ceramics with improved piezoelectric and dielectric properties or good low-temperature plasticity requires Li_2CO_3 as one of the sintering aids [1]. Glass-fibre compositions typically used for fire resistant blankets or containers to provide high burn-through resistance at high temperatures of 1316°C and higher contain Li_2O [2], one of the products prepared from Li_2CO_3 . The amount of Li consumed as glass and ceramic additives reaches about 18 % [3]. There are plenty of other uses of Li. It is a part of lightweight alloys for automotive, aircraft and

aerospace industry; it lowers the temperature of the bath in the electrolysis of molten Al_2O_3 in the production of Al; it is used in pharmacy, lubricants, air conditioners and others. The major uses are shown in the Figure 1.

Since 2007, the most important and the fastest growing area of lithium consumption are the lithium-containing batteries. These are extensively used in small electronic devices like cellular phones, cameras, watches, signal devices etc. as well as in laptops. Lithium batteries are increasingly substituting other batteries, so their con-

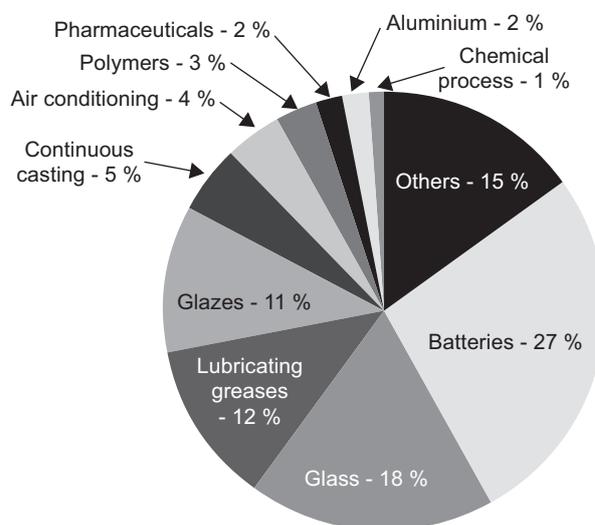


Figure 1. Main uses of lithium [4].

sumption is constantly expanding. The use of lithium batteries has recently been driven by significant growth in transportation. It is estimated that the penetration of plug-in hybrid (PHEV), electric (EV) and hybrid (HEV) vehicles into the market in 2020 will be at 20 % [5]. However, the future demand for lithium in transportation as a preferred medium of energy storage is difficult to predict as no one actually knows just how enthusiastic the trend will be. Nevertheless, no matter how rapidly the demand for lithium will be growing, it is necessary to assure lithium sources and production capacities.

Today, the most of lithium is produced from brines because it is much cheaper than and technologically not as difficult and energetically not as demanding as the production from Li-bearing ores. The brines are found mainly in South America in Chile, Bolivia and Argentina. The largest producer of Li_2CO_3 is the Chilean company SQM covering some 30 % of the market. The world production of lithium reached ca. 18,000 tonnes (95,000 tonnes of equivalent Li_2CO_3) in 2010. Price was ca. 4,500 US\$/tonne in 2010 [6].

With growing demand for lithium, it is expected that some of the alternative sources of lithium will become economically viable. Spent Li batteries are one of such sources even though their recycling is still very limited. Their usage as a Li source is not only connected with possible lithium shortage in the future, but also with the fact that their disposal may become a problem due to the presence of anodic Li which is flammable when exposed towards water or air [7].

In our previous studies [8, 9], we aimed at obtaining Li_2CO_3 from zinnwaldite concentrate with 1.21 % Li and 0.84 % Rb. This concentrate was prepared from zinnwaldite wastes (0.21 % Li, 0.20 % Rb), which originated from dressing Sn-W ores mined in the past in the Czech Republic in Cinovec area. For the processing of the concentrate, gypsum and limestone methods were applied. Gypsum method [8] is based on roasting the concentrate with a mixture of CaSO_4 and $\text{Ca}(\text{OH})_2$ at 950°C, water leaching the obtained calcine at 90°C, solution purification and precipitation of Li_2CO_3 using K_2CO_3 as an precipitation agent. Limestone method [9] consists of roasting the concentrate with CaCO_3 followed by water leaching at 95°C, carbonization of alkaline leach liquor by CO_2 bubbling, solution refining and controlled crystallization of Li_2CO_3 during water evaporation. Both methods make possible to obtain water-washed lithium carbonate salts containing at least 99.5% Li_2CO_3 without applying any recrystallization stages.

The aim of this study was to propose and verify on a laboratory scale simple technologies leading to obtaining Li_2CO_3 from wastes such as spent primary Li/MnO₂ batteries and alkaline lithium-containing wastewater from the production of liquid rubber. Primary Li/MnO₂ batteries use metallic lithium as the anode. The cathode consists of MnO₂ with carbon particles added for improved conductivity. The most common electrolytes

with the system are LiClO_4 or LiCF_3SO_3 in a mixture of propylene carbonate (PC) or dimethoxyethane (DME). The overall cell reaction is

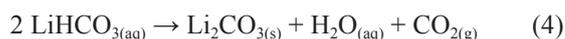


Processing of spent Li/MnO₂ batteries involves roasting the batteries in a vacuum furnace at 650°C, followed by selective leaching of Li_2CO_3 from calcined electrode material in distilled water at ambient temperature and controlled crystallization of pure Li_2CO_3 during water evaporation.

Alkaline wastewaters from the production of liquid rubber contain LiOH. From such solution Li may be precipitated using CO_2 according to the reaction (2).



Lithium carbonate dissolves in water at lower temperatures and in the presence of CO_2 to form more soluble LiHCO_3 according to the reaction (3). LiHCO_3 converts back to Li_2CO_3 at temperatures above 90°C, reaction (4).



Low solubility of Li_2CO_3 especially at higher temperatures compared with that of $\text{LiOH} \cdot \text{H}_2\text{O}$ and other alkali metals carbonates makes possible to separate relatively pure Li_2CO_3 without any further refining [10].

Processing of alkaline waste water in this study comprises condensation up to lithium concentration of 12-13 g/L, conversion of alkaline solution to carbonate solution using excess of bubbled CO_2 at 40°C, heating the solution at 95°C during which soluble LiHCO_3 is transformed to poorly soluble Li_2CO_3 whilst most soluble impurities remain in the solution.

EXPERIMENTAL

Processing of Li/MnO₂ batteries

Spent Li/MnO₂ batteries, which were button cells from different suppliers, were processed according to the flow sheet in Figure 2.

Batteries were roasted at temperatures 450-750°C for 1 h in a vacuum furnace to remove toxic volatile metals and organic compounds. After the completion of roasting the calcines were cooled in the atmosphere. The powder calcined electrode materials were then separated from burst metallic battery casings by vibration screening. Calcines after their standard grinding were leached in 2 L closed glass reaction vessel. Mixing was accomplished by means of an impeller. During leaching, samples were withdrawn at selected time intervals to determine the reaction rate of lithium dissolution. Lithium concentrations in the filtrates were established using AAS method. After the completion

of leaching experiments, leach residues were filtered, dried, weighed and subjected to the chemical and XRD analysis.

At selected time intervals during the leaching, samples were withdrawn to determine concentration of Li in the solution using AAS method. Leach residues were filtered, dried, weighed and analysed chemically and by XRD. Leaching was performed under following conditions: distilled water, liquid-to-solid ratio (l:s) 20-30:1, laboratory temperature, reaction time of 1-3 h. The leaching temperature and the values of l:s were determined from data for Li_2CO_3 solubility in water, which showed a decrease in solubility from 15.4 g/L at 0°C to 7.20 g/L at 100°C [10].

Li_2CO_3 was separated from the leached solutions by evaporation under standard mixing at the boiling temperature. During the evaporation, the influence of the amount of removed water on the purity of Li_2CO_3 obtained was examined. Samples of suspension were withdrawn at selected volumes of the solutions processed and after the filtration both liquid and solid phases were subjected to chemical analysis. The solid phases were characterized by XRD analysis.

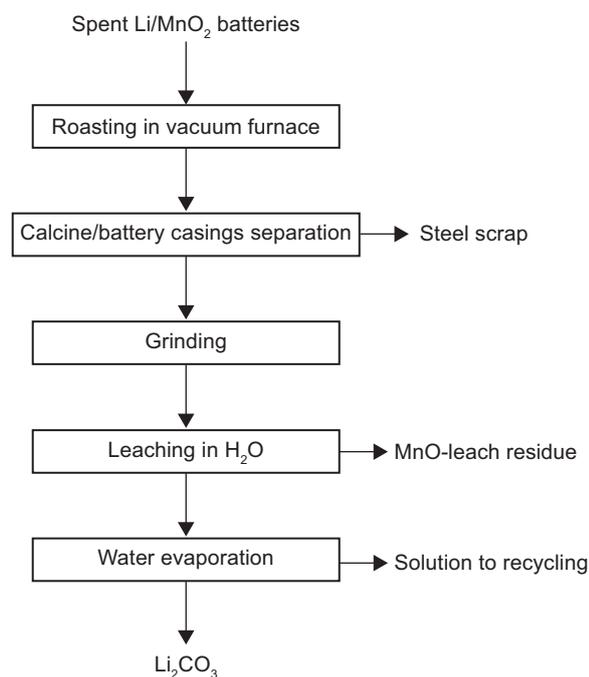


Figure 2. Flowsheet of processing spent Li/MnO₂ batteries.

Processing of wastewater

Lithium-containing alkaline wastewater originated from the production of liquid rubber, which is a product of anionic polymerization of butadiene in a polar solvent in the presence of organolithium initiator. Lithium passes to wastewaters from organo-lithium in a hydroxide form. Concentration of Li and impurities in the processed wastewater is given in Table 1.

Processing of lithium-containing waste water is illustrated in Figure 3. Before the Li_2CO_3 precipitation, samples of wastewater solution were condensed up to lithium concentration of 12-13 g/L in a common distillation apparatus. During the condensation, present organic compounds were evaporated. Two-step Li_2CO_3 precipitation was performed in a thermostated standard stirred glass vessel equipped with gas flow meter, gas fritted inlet, thermometer and water cooler. In the first step, evaporated solutions were bubbled with excess CO_2 at 40°C for 2 h to obtain solution of LiHCO_3 . After the completion of the carbonization, gas fritted inlet was removed from the vessel and the solution was heated up to 95°C and maintained at this temperature for 3 h. After the completion of Li_2CO_3 crystallization solid phases were filtered off, dried, weighed and subjected to the chemical and XRD analysis. During the whole procedure, samples of solutions were withdrawn at selected time intervals to determine lithium concentration.

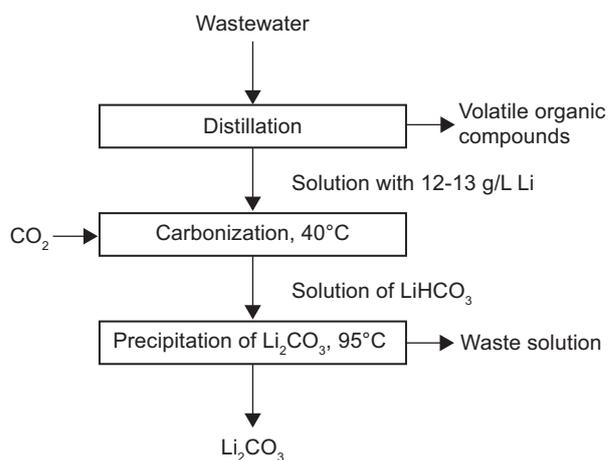


Figure 3. Flowsheet of processing Li-containing wastewater.

Table 1. Content of Li and impurities in the wastewater from the liquid rubber production.

| Concentration of elements/compounds in the processed wastewater (mg/L) | | | | | | | | | |
|--|------|------|------|-----|-----|-----|-------|------|------|
| Li | Na | Fe | Si | Al | Zn | K | MeOH | MTBE | PrOx |
| 6790.0 | 31.0 | 12.2 | 20.3 | 2.0 | 5.4 | 1.0 | 587.0 | 1.0 | 1.0 |

MeOH – methylalcohol; MTBE – methylterbutylether; PrOx – propyleneoxide

RESULTS AND DISCUSSION

Processing of Li/MnO₂ batteries

Depending on the roasting temperature, calcines contained 47-55 % Mn, 4.3-5.5 % Li and insignificant amounts of impurities, such as Fe, Zn, Ni, Na, Ni and Cr, Table 2. It is obvious that increasing the roasting temperature above 550°C resulted in the volatilisation of lithium from the calcine.

Table 2. Average chemical composition of the calcined electrode materials.

| Calcination temperature | Elemental content (wt.%) | | | | | | |
|-------------------------|--------------------------|-------|------|------|------|------|------|
| | Li | Mn | Fe | Zn | Na | Ni | Cr |
| 450°C | 5.11 | 49.42 | 0.13 | 0.11 | 0.29 | 0.18 | 0.14 |
| 550°C | 5.45 | 47.46 | 0.07 | 0.19 | 0.17 | 0.14 | 0.13 |
| 650°C | 4.83 | 51.26 | 0.16 | 0.22 | 0.17 | 0.14 | 0.23 |
| 750°C | 4.26 | 55.42 | 0.31 | 0.18 | 0.14 | 0.13 | 0.50 |

The calcines contained according to XRD analysis two dominate phases: manganosite (MnO) and zabuyelite (Li₂CO₃). Small amounts of graphite (C) were also present, at all temperatures. The calcine formed at 450°C contained a certain quantity of LiMnO₂ while calcinations at 750°C provided small amount of LiOH·H₂O. We suppose that during roasting of the batteries in the vacuum furnace, the manganese phases, LiMnO₂ and non-reacted MnO₂ are reduced to MnO by graphite and by the residual Li metal. The resultant CO₂ and Li₂O then react to form Li₂CO₃. The amount of the LiMnO₂ transformed to MnO and Li₂CO₃ increases up to approximately 700°C. The presence of LiOH·H₂O after calcination at 750°C is caused by Li₂CO₃ decomposition above about 700°C and Li₂O further reaction with atmosphere moisture after the sample is cooled down.

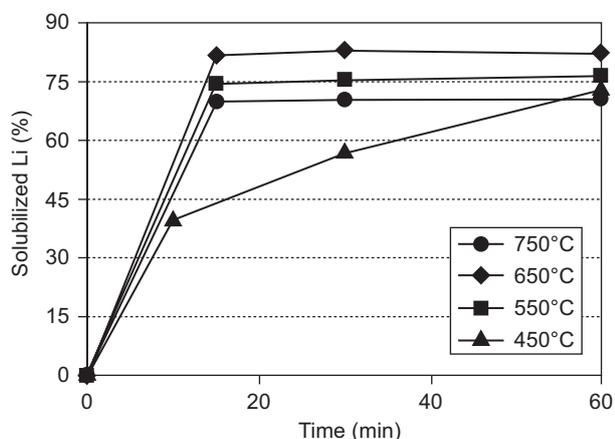


Figure 4. Dependence of Li extraction from calcined electrode material on different roasting temperature at $l : s = 25 : 1$.

The lithium extraction efficiency as a function of roasting temperature obtained at $l : s = 25 : 1$ is shown in Figure 4. The calcines obtained at 550, 650 and 750°C exhibit similar characteristic with Li extraction practically completed within 20 min. Lithium dissolution from the 450°C calcine was somewhat slower due to the presence of the LiMnO₂ phase, but reached approximately 80 % after 3 h.

The extent of lithium extraction passed through an apparent maximum about 80 % at 650°C. The leach residues contained 0.7-1.3 % Li, 60-70 % Mn and 7-10 % C depending on the calcination temperature. Only the minor MnO phase and a small amount of graphite were determined by XRD analysis. There was no indication of the identity of the insoluble Li-bearing phase in the XRD. This is probably due to its low abundance, however, the most likely phase is unreduced LiMnO₂.

Limited solubility of Li₂CO₃ in water caused lower Li dissolution by leaching the 650°C calcine at $l : s = 20 : 1$. Increasing $l : s$ to 30:1 did not enhance the Li extraction efficiency. Concentration of Li in the filtrates ranged from 1.83 to 1.31 g/L depending on the increasing liquid-to-solid ratio.

Extracts originating from leaching calcined electrode materials at 650°C were subjected to Li₂CO₃ crystallization by the controlled water evaporation. The processed solutions prepared at $l : s = 25 : 1$ contained on average 1.31 g/L Li. The influence of the degree of solution evaporation on the purity of separated Li₂CO₃ is shown in Figure 5.

Lithium salt containing at least of 99.5 % Li₂CO₃ crystallised until about 95 % of water was evaporated when more soluble salts, namely sulphates and chlorides of K, Na, Ca and probably sodium silicate started to crystallise. However, the purity of Li₂CO₃ crystals obtained after 95 % water evaporation could be raised by water washing of the original Li₂CO₃.

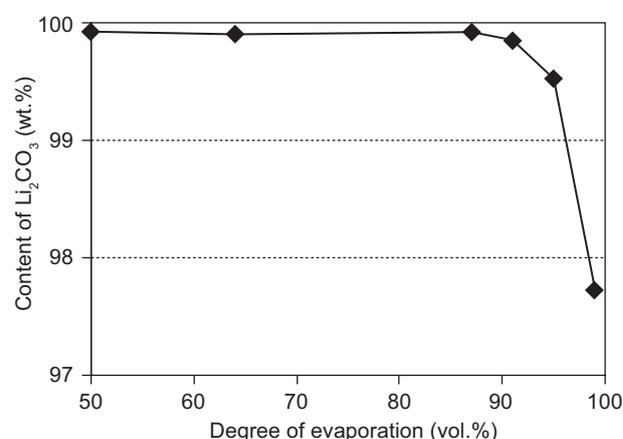


Figure 5. Dependence of Li₂CO₃ purity on the volume of evaporated solution.

The method of processing lithium-containing waste water from the production liquid rubber described in this paper was patented [11].

Processing of wastewater

Organic compounds present in the wastewater were evaporated during distillation. The course of carbonization of evaporated wastewater samples (exp.1-6) and the subsequent Li_2CO_3 crystallization from these solutions is illustrated in Figure 6.

Approximately 90 % Li_2CO_3 crystallized from carbonized solutions after 30 min of heating the processed solutions. The residual Li concentration in the mother liquors ranged from 1.83 to 2.00 g/L. This corresponds to the theoretical solubility of Li_2CO_3 . Lithium carbonate salts obtained contained more than 99.7 % Li_2CO_3 and negligible amounts of Si, Fe, Zn and Al. The detailed description of the procedure of wastewater processing is given in our previous study [12].

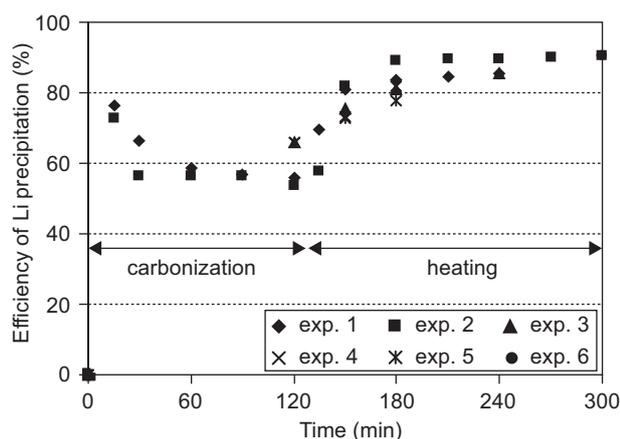


Figure 6. Course of lithium precipitation from condensed solutions.

CONCLUSIONS

Lithium carbonate containing at least 99.5 % Li_2CO_3 can be readily recovered both from spent Li/ MnO_2 batteries and lithium-containing wastewater from the production of liquid rubber without any further refining. Developed and verified processes are based on simple and environmental friendly operations. Proposed processing of spent Li/ MnO_2 batteries makes possible deactivation and detoxification of spent batteries in

one technological step. Toxic compounds are collected in off-gases, from which they could be ecologically separated. In the same step - during roasting of batteries, residual metallic lithium or cathode lithium could be transformed to Li_2CO_3 and manganese (IV) oxides to MnO . Li_2CO_3 can be selectively dissolved in water at the ambient temperature and separated by a simple controlled crystallization. The recovery Li_2CO_3 from alkaline lithium-containing wastewater is based only on condensation-precipitation steps. Organic compounds are safely removed during wastewater condensation under simultaneously increasing lithium concentration from ca. 6 g/L to 12-13 g/L which is necessary to obtain 90 % yield of Li_2CO_3 by water evaporation. Formation of soluble LiHCO_3 in the first precipitation step makes possible to reach efficient carbonization of the original waste water and to avoid technical problems caused by filling the gas fritted inlet of CO_2 with sparingly soluble Li_2CO_3 .

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