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Recovery of Lithium Hydroxide from Spent Lithium Carbonate using Crystallizations

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Abstract: Recovery of LiOH from the spent Li_2CO_3 used as absorbent for carbon dioxide in breathing apparatus was successfully explored by precipitation and crystallization. A lithium hydroxide solution was prepared by precipitation of calcium carbonate using reaction of spent Li_2CO_3 and calcium hydroxide. The effects of the operating conditions on the reaction were investigated. Conversion of calcium carbonate was about 95%. Lithium hydroxide monohydrate from lithium hydroxide solution was obtained in batch evaporative crystallization. The effect of the evaporation rate on crystal morphology was investigated. The evaporation rates were affected to control size and yield of crystals. Eventually, the purity of crystals was above 99 wt% and yield was about 80%.

Keywords: Crystallization, separation, lithium, recovery

INTRODUCTION

A pellet of lithium hydroxide is presently being used as an effective CO_2 absorbent in closed ecological systems such as submarines and space vehicles and portable life support systems (1). In these applications, air or oxygen laden with carbon dioxide from human or animal respiration is forced through a bed of lithium hydroxide granules. The carbon dioxide is removed and the carrier

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gas is returned to the environment (2). One gram of anhydrous lithium hydroxide absorbs 450 mL of carbon dioxide, so that 750 g of lithium hydroxide is sufficient to absorb the carbon dioxide generated by one person in one day.

In the closed space, the lithium hydroxide is converted into lithium carbonate, lithium oxide, lithium monohydrate etc., in which lithium carbonate is dominated. The spent Li_2CO_3 is used as a source of low-grade lithium carbonate, but is never recycled as a CO_2 adsorbent.

Lithium hydroxide is produced by the digestion of lithium ore with alkali (3). On the other way, reaction between lithium carbonate and calcium hydroxide is used (1, 4):

$$Li_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + 2LiOH \tag{1}$$

This method has advantages in economic aspects due to higher yield and purity than the digestion of lithium ore. It yields solutions containing up to 3.5% lithium hydroxide (4). Attempts to work at higher concentration lead to loss of lithium carbonate in the calcium carbonate residue, because the solubility of lithium carbonate is reduced in the presence of lithium hydroxide. The precipitated calcium carbonate is removed, and the lithium hydroxide monohydrate is crystallized from the mother liquor by evaporation. Therefore precipitation and crystallization technologies should be understood to recycle the spent lithium carbonate.

The aims of this study are to prepare lithium hydroxide by recovery of lithium hydroxide from spent lithium carbonate in precipitation and evaporative crystallization. The reaction of Li_2CO_3 and $Ca(OH)_2$ in aqueous solution was examined to obtain LiOH aqueous solution. The effects of reaction time and feed concentration in reaction crystallization were investigated. Evaporative crystallization of lithium hydroxide monohydrate in lithium hydroxide solution was examined. The effects of the evaporation rate and the cooling rate on the growth rate and particle size were investigated.

EXPERIMENTAL

Materials and Apparatus

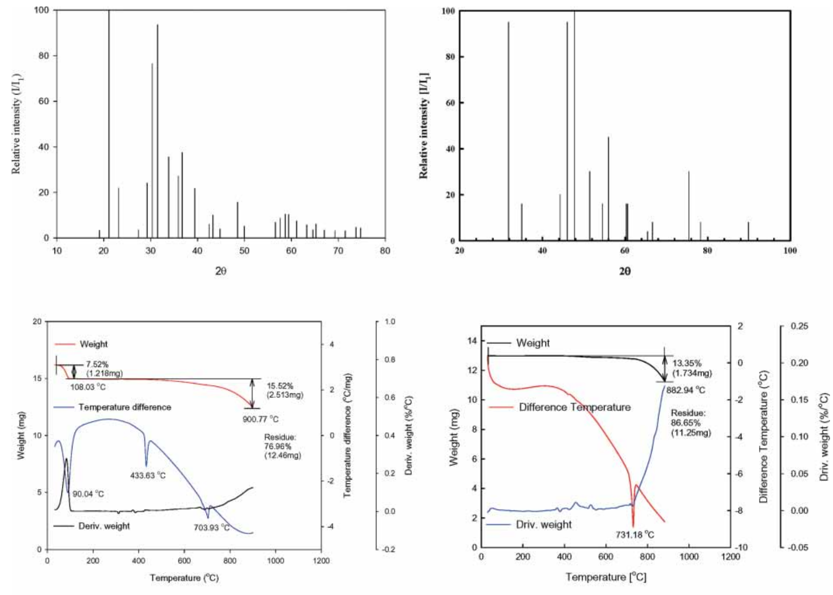
Spent Li_2CO_3 pellet (pellet size: 5×5 mm) was to be used as absorbent for carbon dioxide in breathing apparatus. Calcium hydroxide ($Ca(OH)_2$) was from DC Chemical Co. Ltd. The water used in this work was triply distilled.

The crystallizer was made of Pyrex glass with a jacketed vessel with a total volume of 2500 mL. It was equipped with an agitator, a marine propeller type with a 60 mm diameter at a set speed of 500 rpm. The temperatures of the inside crystallizer and the thermostat bath were recorded by digital temperature recorder. The temperature of the crystallizer was controlled by PID temperature controller with an error range of ± 0.05 K.

Experimental Procedure and Analysis

Figure 1 shows the flow sheet for the recovery of lithium hydroxide from spent lithium carbonate. The experimental procedure is divided into two steps: precipitation and evaporative crystallization. In precipitation step, spent lithium carbonate was dissolved for 1 hr at 10°C, 500 rpm (solubility of lithium carbonate is 1.36 g/water 100 g at 10°C) (5). Calcium hydroxide ($Ca(OH)_2$) is added in the solution. The reaction is carried out for 3 hours. The reaction was carried out by mixing 20 g of spent $LiCO_3$, 20 g of $Ca(OH)_2$ in 2000 g of water at 90°C. $CaCO_3$ was precipitated during the reaction and was removed from mother liquor using filter. Content of Ca^+ and Li^+ in solution was analyzed with the elapsed time by ICP with accuracy of ± 30 ppb.

In crystallization step, the lithium hydroxide monohydrate ($LiOH \cdot H_2O$) was obtained by evaporation of water from the filtrate obtained after filtration of the $CaCO_3$ crystals. The evaporation rate was controlled to generate the supersaturation. Water evaporated is in the range of 80 to 90% of water fed, which depends on yield of product. Evaporation rate is ranged from 0.01 L/h to 1 L/h. The lithium hydroxide monohydrate ($LiOH \cdot H_2O$) crystals obtained were analyzed by XRD. After the lithium monohydrate was dried for 3 hr in furnace at 500°C, LiOH crystals were obtained. Li content in solution was measured by AA analysis.



(spent Li_2CO_3) (Li_2CO_3)

Figure 1. XRD patterns and TG-DTA curves of Li_2CO_3 and spent Li_2CO_3.

Analysis equipments used in an experiment were as follows: Atomic Absorption Spectrometer (AA; Perkin-Elmer 2380 AAS) and Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP AES; Jovin Yvon Ultima-C, X-Ray Diffractometer (XRD; Rigaku D/MAX-2000), Scanning Electron Microscope/Energy Dispersive X-Ray Spectrometer (SEM/EDS), Image Analyzer (VIDAS, Karl Zeiss) and Simultaneous TGA-DTA (Mode: SDT 2960).

RESULTS AND DISCUSSION

The production of lithium hydroxide monohydrate has been carried out by the reaction between lithium carbonate and calcium hydroxide. The precipitated calcium carbonate was removed, and then lithium hydroxide monohydrate was crystallized from the mother liquor by evaporation under vacuum. Therefore, it is necessary to know the mechanisms of reaction crystallization between Li_2CO_3 and $Ca(OH)_2$ and of evaporative crystallization with the LiOH solution.

Spent Li_2CO_3

Figure 2 shows its XRD Patterns and TG-DTA curves of spent Li_2CO_3 and standard Li_2CO_3. It was found to be converted mainly into Li_2CO_3 from the

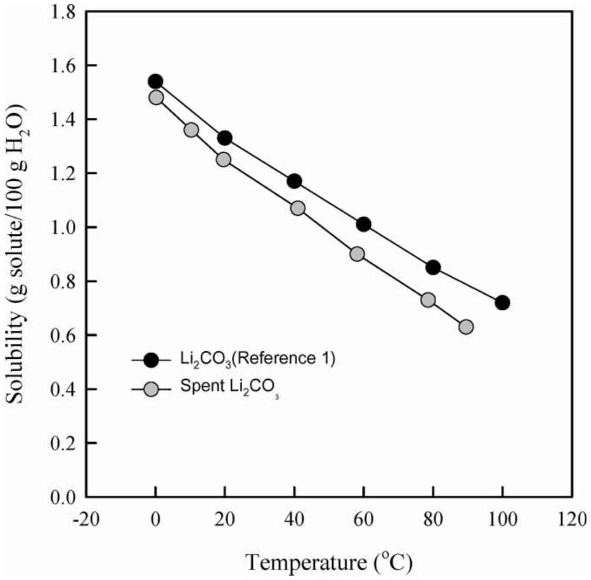


Figure 2. Solubility of Li_2CO_3 and spent Li_2CO_3.

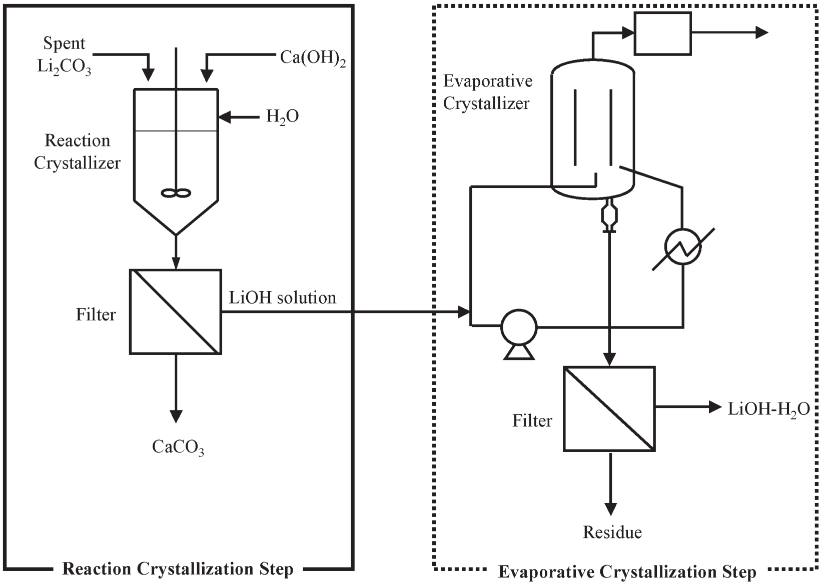


Figure 3. Flow sheet for the recovery of lithium hydroxide from spent lithium carbonate.

result of TG-DTA analysis. Decomposition of Li_2CO_3 starts at 733.26°C. CO_2 of 5.151 mg was removed in a standard reagent. Peaks in decomposition of crude spent Li_2CO_3 were found at the temperatures 90.04°C, 433.63°C, and 703.93°C due to presence of Li_2CO_3, $LiOH \cdot H_2O$, and LiOH. As can be seen in XRD patterns, spent Li_2CO_3 is different with Li_2CO_3 patterns and contains LiOH, $LiOH \cdot H_2O$, and Li_2CO_3. Figure 3 shows the solubility of spent Li_2CO_3 and standard Li_2CO_3 in water. Solubility of spent Li_2CO_3 is lower than that of standard Li_2CO_3, which results from inclusion of LiOH and $LiOH \cdot H_2O$.

Precipitaion of $CaCO_3$

Overall reaction equation in reaction crystallization is as follows.

$$Li_2CO_3 + Ca(OH)_2 + H_2O \longrightarrow CaCO_3 \downarrow + 2LiOH + H_2O \qquad (2)$$

Solubility of Li_2CO_3 decreases with increasing LiOH. The created lithium hydroxide (LiOH) reduces amount of solubility of Li_2CO_3. Therefore, the pH for the hydration lithium withdrawal is considered. When Li_2CO_3 is dissolved in water,

$$2\mathrm{Li}^+ + \mathrm{CO}_3^{2-} + \mathrm{H_2O} + \mathrm{CO_2} \longleftrightarrow 2\mathrm{Li}^+ + 2\mathrm{HCO}_3^- \tag{3}$$

$$\mathrm{H_2O} + \mathrm{CO_2} \longleftrightarrow \mathrm{H_2CO_3} \longleftrightarrow \mathrm{H}^+ + \mathrm{HCO}_3^- \longleftrightarrow 2\mathrm{H}^+ + \mathrm{CO}_3^- \tag{4}$$

$$\frac{[\mathrm{H}^+][\mathrm{CO}_3^{2-}]}{[\mathrm{HCO}_3^-]} = 10^{-10.4} \tag{5}$$

Consequently, from the reaction with the dissociation constant, if pH of aqueous solution is below 10.5, Li_2CO_3 can be formed.

$$\mathrm{Li_2CO_3(s)} \longleftrightarrow 2\mathrm{Li}^+\mathrm{(aq)} + \mathrm{CO}_3^{2-}\mathrm{(aq)} \tag{6}$$

$$[\mathrm{Li}^+]^2[\mathrm{CO}_3^{2-}] = 8.15 \times 10^{-4} \tag{7}$$

When $Ca(OH)_2$ is added in Li_2CO_3 solution, pH is changed.

$$\mathrm{Ca(OH)_2} \longleftrightarrow \mathrm{Ca}^{2+}\mathrm{(aq)} + 2\mathrm{OH}^-\mathrm{(aq)} \tag{8}$$

$$\mathrm{Ca(OH)_2} + \mathrm{CO}_3^{2-} \longleftrightarrow \mathrm{CaCO_3(s)} + 2\mathrm{OH}^-(\mathrm{pH} = 14.3) \tag{9}$$

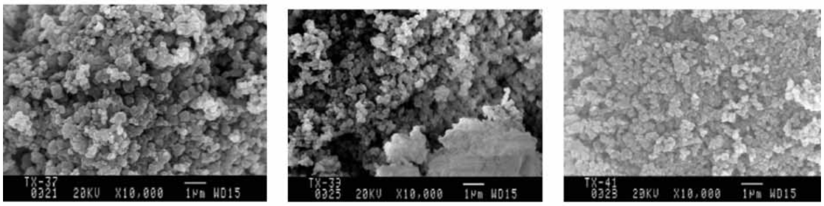
$$\frac{[\mathrm{OH}^-]^2}{[\mathrm{CO}_3^{2-}]} = 2 \times 10^3 \tag{10}$$

Therefore, calcium carbonate is formed in crystal phase and LiOH is formed in mother liquor at $\mathrm{pH} = 14.3$. LiOH in mother liquor (LiOH solution) can be crystallized by evaporative crystallization.

Figure 4(a) shows SEM photographs of crystals obtained with the elapsed reaction time. Figure 4(b) shows the XRD patterns of crystals precipitated during the reaction. From the analysis of XRD patterns, crystals were identified as a calcite. Generally such a quick mixing generates higher supersaturation than slow mixing. Thus, it supports that the calcite crystal preferentially crystallizes at relatively high supersaturation (6). The crystallite size of the obtained $CaCO_3$ is approximately 1 μm, increases with the reaction time. The effect of the reaction time on the crystallite form is negligible.

Figure 5 shows plots of Li^+ content inside $CaCO_3$ crystals against the reaction time. As can be seen, Li content included in the $CaCO_3$ crystals decreases with increasing the reaction time. This means that at the beginning of $CaCO_3$ precipitation Li is largely entrapped due to the maximum supersaturation for precipitation, which results from maximum concentration of reactants. When the reaction time passed above 30 min, it was found that the precipitation of $CaCO_3$ was completed. After three hours elapsed in the reaction, the lithium ion content included in crystalline particles was decreased until 0.5 ppm.

(a) SEM photographs



1 hr 2 hr 3 hr

(b) XRD patterns

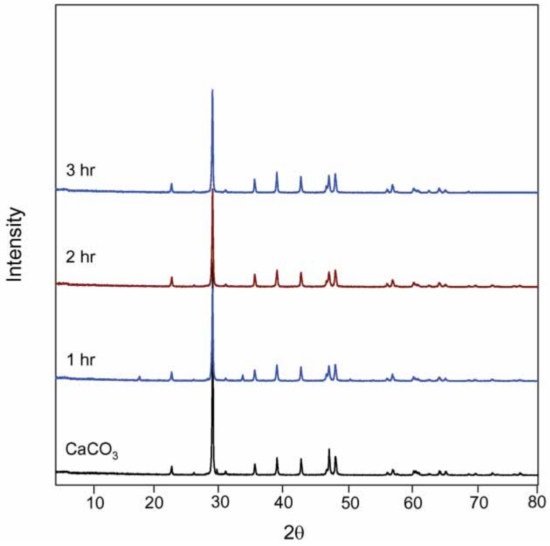


Figure 4. (a) SEM photographs and (b) XRD patterns of obtained $CaCO_3$ crystals with elapsed reaction time.

Figure 6 illustrates the content of Ca^+ in mother liquor (LiOH solution) with the elapsed time in the reaction. Ca ion content decreases rapidly at the beginning of reaction. When the reaction time passed two hours, the content of Ca^+ was about 1 ppm in the solution. Eventually, conversion of $CaCO_3$ in the reaction was above 99 wt%.

Crystallization of $LiOH \cdot H_2O$

By evaporating residual solution obtained after filtering $CaCO_3$ precipitated in the reaction, $LiOH \cdot H_2O$ crystals are supersaturated and crystallized. Evaporation rate is an important parameter in evaporation crystallization.

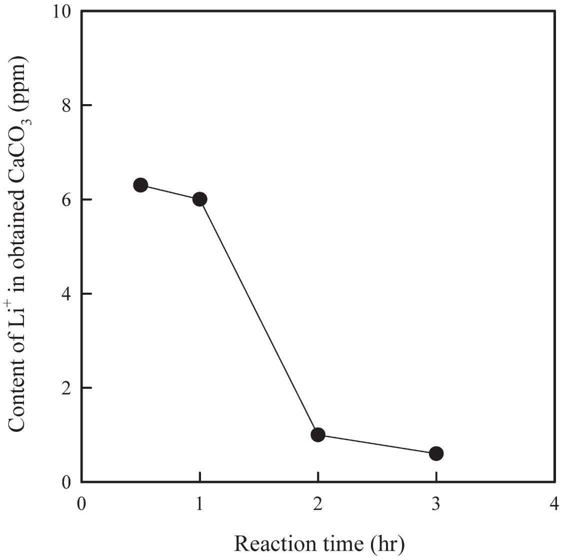


Figure 5. Content of Li$^+$ in crystals obtained according to reaction time.

Figure 7 shows the photos of the crystals obtained by evaporation crystallization operating at an evaporation rate of 100 mL/h with the elapsed time. Crystals obtained after 3 h have a monoclinic shape.

Figures 8(a) and 8(b) show the content of Ca$^+$ and XRD data for the crystals obtained in evaporative crystallization, respectively. As can be seen

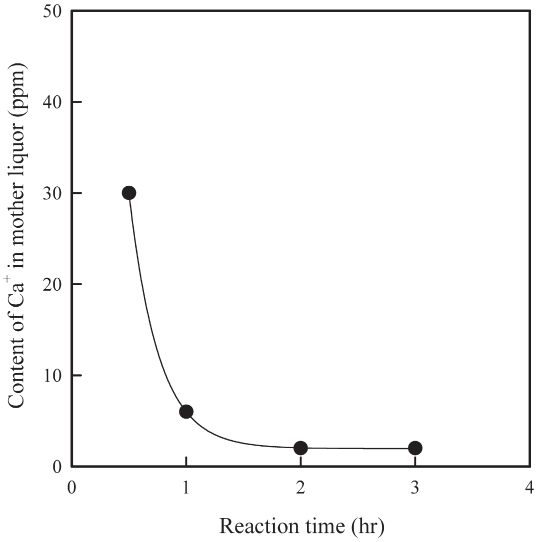


Figure 6. Content of Ca$^+$ in mother liquor according to reaction time.

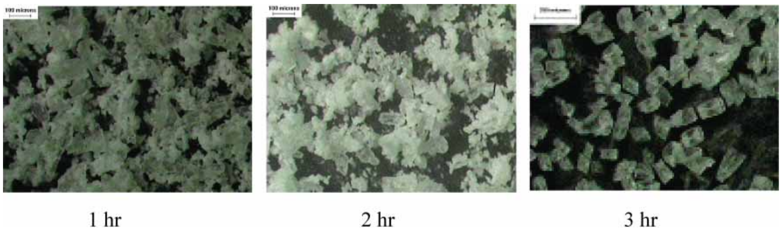
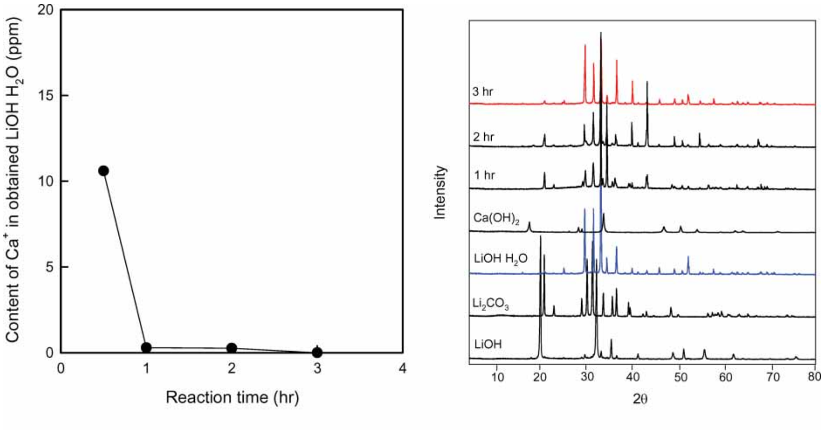


Figure 7. Photos of the crystals obtained by evaporative crystallization with elapsed time.

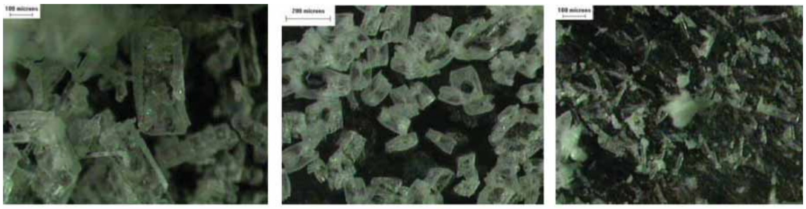
in these figures, the Ca content in the crystals decreased and disappeared completely within 1 h. XRD patterns of obtained $LiOH \cdot H_2O$ suggests crystals is changed completely into $LiOH \cdot H_2O$ with a trace of lithium carbonate after 3 h in crystallization. Crystal size is increased with the elapsed time in the evaporation crystallization. Final $LiOH \cdot H_2O$ crystals contained the 0.4 ppm of calcium ion. High purity of lithium hydroxide monohydrate was achieved through the precipitation and crystallization of calcium hydroxide and lithium carbonate in distilled water. The purity of LiOH was above 99% and the yield was about 80%.

Figure 9 shows the optical photographs of the crystals obtained in the evaporation rates of 0.01, 0.1, and 1 L/h. When 0.1 L/h of the evaporation rate was carried out, $LiOH \cdot H_2O$ crystals have a polygonal shape and include 1.4 ppm of calcium. In 1 L/h of evaporation rate, $LiOH \cdot H_2O$ crystals have a needle-like shape and the impurity content of $LiOH \cdot H_2O$ crystals was 1.8 ppm. The larger crystal size results from the lower



(a) (b)

Figure 8. (a) Content of Ca^+(A) and (b) XRD patterns of crystals obtained ($LiOH \cdot H_2O$) with elapsed reaction time.



10 mL/h 100 mL/h 1000 mL/h

Figure 9. Photos of crystals obtained with various evaporation rates.

evaporation rate, which leads to the lower supersaturation. Evaporation rate of the saturated solution affect directly the supersaturation rate (7–9). The higher evaporation rate induces the higher supersaturation rate, which results in the more impure crystals with a needle-like shape. The morphology of crystals is found to be monoclinic. Higher evaporation rate leads to growth of crystals with larger aspect ratio. Crystallization at an evaporation rate of 0.1 L/h is desirable for crystals of 150 μm with monoclinic form.

CONCLUSIONS

The effects of the operating conditions in reaction and evaporative crystallizations were investigated. Conversion of calcium carbonate was about 95%. Lithium hydroxide monohydrate from lithium hydroxide solution was obtained from evaporative crystallization. The evaporation rate was affected to control the size and the yield of crystals. Purity of lithium hydroxide monohydrate crystals was above 99 wt%, and its yield was above 80%. Recovery of LiOH from spent Li_2CO_3 used as absorbent for carbon dioxide was successfully explored by precipitation and crystallization.

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