Hydrometallurgy 146 (2014) 142–148

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Precipitation behavior of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ from $CaCl_2$, $MgCl_2$, and $MnCl_2$ in NaOH-H_2O solutions and study of lithium recovery from seawater via two-stage precipitation process

Namil Um [a],*, Tetsuji Hirato [b]

[a] Environmental Resources Research, National Institute of Environmental Research, Hwangyeong-ro 42, Seo-gu, Incheon 404-708, South Korea
[b] Department of Energy Science and Technology, Graduate School of Energy Science, Kyoto University, Kyoto 611-0011, Japan

ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form 5 April 2014
Accepted 8 April 2014
Available online 18 April 2014

Keywords:
Lithium recovery
Seawater
Lithium carbonate
Chemical modeling
Hydrometallurgical method

ABSTRACT

This study describes a hydrometallurgical process to investigate the recovery of lithium from seawater using devised total process including an adsorption process with manganese oxide adsorbent and a precipitation process. First, precipitation experiments on $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ from $CaCl_2$, $MgCl_2$, and $MgCl_2$ in NaOH-H_2O solutions were carried out under various conditions of reaction temperature (25–90 °C), NaOH concentration (7–14 pH), and initial amount of $CaCl_2$, $MgCl_2$, and $MnCl_2$ (10 and 100 mmol/dm^3). The obtained results showed that there was a need to divide the precipitation process into two steps based on the precipitation characteristics of the target elements in NaOH (or HCl)-H_2O solutions. These two steps consist of a first stage with precipitation of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ by NaOH and a second stage with Li_2CO_3 recovery by neutralization using HCl, carbonation using Na_2CO_3, and concentration using evaporation. Chemical modeling with OLI-Systems® software was used to interpret the precipitation behavior of target elements in the first and second stages; it was compared with available experimental data and good agreement was found. On the basis of the above data, it was possible to separate Ca, Mg, and Mn under pH values ranging from 11.5 to 12.5 in the first stage after the process of seawater adsorption with manganese oxide adsorbent and to recover crystalline Li_2CO_3 with high purity (over 99%) carbonated by Na_2CO_3 in the second stage, involving neutralization by adjusting the pH value in the range of 6–8 and evaporation at 100 °C to obtain the product with high yield.

1. Introduction

Since less than 100 tonnes of lithium carbonate equivalent was consumed per annum in the early 20th century, it could be used without difficulty to achieve improved applications in various fields for batteries, lubricating grease, frit, glass, air-conditioning, aluminum, pharmaceuticals, polymers, and other products (Ebensperger et al., 2005). Now, lithium is recovered from four types of resources, namely, minerals, brine, clay, and seawater, which contain about 64 million tonnes (with the exception of seawater with more than 224 billion tonnes) in total, and lithium carbonate, lithium hydroxide, lithium chloride, lithium metal, and other lithium-containing products have been produced from these resources using physical and chemical treatments, such as particle size separation, flotation, solvent extraction, adsorption, and precipitation methods (Yaksic and Tilton, 2009). According to Bale et al. (Bale and May, 1989), lithium could be recovered from pyroxene minerals as a milled pre-concentrate for the bulk glass industry, and as a flotation concentrate for the specialty glass and pyroceramic industry. In the case of lithium extraction focused on the treatment of Salar de Uyuni brine, high-purity lithium carbonate was recovered using a precipitation method (An et al., 2012). Froth flotation and magnetic separation were also used to recover lithium from clay (Siame and Pascoe, 2011). In addition, an adsorption method is suitable for lithium recovery from seawater, which is considered as a vast source, although its lithium concentration is very low, that is, 0.17 mg/dm^3, because inorganic ion-exchange materials, such as spinel-type hydrous manganese oxides, as adsorbents show high selectivity to lithium ions (Angino and Billings, 1965; Riley and Tongudai, 1964).

However, the adsorption method has some demerits in terms of the separation and recovery of high-purity lithium from seawater. Undesired species, such as Ca, Mg, Mn, Na, and K, are adsorbed along with Li by the adsorbent (Chitrakar et al., 2001; Umeno et al., 2002; Yoshizuka et al., 2006) and another method is needed to separate these materials. Development of a complete process scheme using a precipitation process as well as an adsorption process is therefore needed for high-purity lithium recovery from seawater. A precipitation process based on the precipitation characteristics of the main elements in the target solutions has to be implemented to separate Ca, Mg, Mn, Na, and K as by-products, leaving behind Li for its subsequent recovery.

---

* Corresponding author.
E-mail address: inhaking96@hotmail.com (N. Um).

http://dx.doi.org/10.1016/j.hydromet.2014.04.006
0304-386X/© 2014 Elsevier B.V. All rights reserved.

Chemical modeling involving multiple chemical equilibria can be used to predict an aqueous processing system with the required temperature and concentration; OLI-Systems® software, which chemically provides for the rigorous computation of the principal thermodynamic properties including Gibbs free energy, enthalpy, entropy, heat capacity and volume in an aqueous electrolyte solution, can be used to fit chemical equilibria of a target material in acidic or alkali solutions (Liu and Papangelakis, 2005a, 2005b; Pazuki and Rohani, 2006). Therefore, in this study, the precipitation behavior of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ from $CaCl_2$, $MgCl_2$, and $MnCl_2$ in NaOH-H_2O solutions was investigated and interpreted by chemical modeling plotted with OLI-Systems® software. The resulting data were calculated to confirm the effects of reaction temperature, NaOH concentration (pH value), initial amount of $CaCl_2$, $MgCl_2$, and $MnCl_2$, and multiple components of Ca, Mg, and Mn on precipitation. Using the obtained data, it was suggested that two-stage precipitation could be adopted for lithium recovery from seawater, using NaOH to separate Ca, Mg, and Mn by precipitation as $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ from target solutions in the first stage, and using Na_2CO_3 to recover Li_2CO_3 precipitate in the second stage involving neutralization and evaporation to obtain a high-purity product.

2. Experimental methods

2.1. Materials

Lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), magnesium chloride (MgCl), and manganese chloride ($MnCl_2$) used in this study were of chemical grade of >99.9% metal basis (Wako Pure Chemical Industries) and the particle size of all reagents was <5 μm.

2.2. Experimental methods

All experiments were carried out by putting the desired amount of each reagent into 150 mL target solutions with various acid or alkali concentrations in a batch-type glass reactor of 300 mL heated at the desired temperature; the reactor was placed on a hot plate stirrer. The solution was stirred by a magnetic stirrer at 650 rpm agitation speed. The control variables used in the experiments were as follows: HCl or NaOH concentration (pH value) and reaction temperature.

To measure the pH of target solutions, hydrogen ion concentration was checked using a pH meter (Horiba, F-52). The samples with appropriate pH and reaction temperature were filtered from solution on a 0.5 μm pore size membrane using a pressure filtration unit. After drying at 45 °C for 24 h, the weight (a) of the precipitate was measured using a balance. The concentration (b) of the target element in the residual solutions after filtration was determined by ICP-AES (Seiko Instruments Inc., SPS7800). The data of (a) and (b) reflected the measurement of precipitate and leachate in both first and second stages of this lithium recovery process.

To identify the crystalline phases of product produced from the final precipitation, the obtained sample was measured using an X-ray diffractometer (PANalytical, X'pert PRO) for mineralogical analysis.

3. Results and discussion

3.1. Precipitation of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ from $CaCl_2$, $MgCl_2$, and $MnCl_2$ in NaOH-H_2O solutions

The chemical reaction in the precipitation of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ is considered to occur according to the following dissolution reaction:

$$\begin{aligned}&MCl_2 + 2OH^- \rightarrow M(OH)_2 + 2Cl^- \\ &M = Ca, Mg, \text{and } Mn.\end{aligned} \tag{1}$$

Under high alkali conditions, the concentration of Ca (or Mg and Mn) exceeds its solubility. Then, Ca (or Mg and Mn) cations under the saturated conditions directly form Ca (or Mg and Mn) hydroxide. Reaction temperature, NaOH concentration (pH value), initial amount of $CaCl_2$, $MgCl_2$, and $MnCl_2$, and multiple components of Ca, Mg, and Mn are the important factors for the precipitation and their effects are discussed in detail below.

3.1.1. Effect of reaction temperature

In order to predict the effect of reaction temperature on the precipitation behavior of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ in Ca-, Mg-, and $MnCl_2$-NaOH-H_2O solutions, the precipitation-pH diagrams at various conditions of reaction temperature and pH value were investigated and are shown in Fig. 1. The initial amount was kept constant at 10 mmol/dm^3. In addition, comparison between experimental values and chemical modeling fitted by OLI-Systems® software was performed. The solid lines represent the resulting chemical modeling as a function of pH value at various reaction temperatures ranging from 25 to 90 °C and were in good agreement with the experimental data across the whole range of pH values. The curves of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$, which exhibited L- and U-forms, were shifted to the left with increasing temperature. These results indicate that it was possible to precipitate $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ at a much lower pH, rather than that at 25 °C, by increasing the reaction temperature from 25 to 90 °C.

3.1.2. Effect of initial amount of $CaCl_2$, $MgCl_2$, and $MnCl_2$

The effect of initial amount of $CaCl_2$, $MgCl_2$, and $MnCl_2$ on precipitation was tested by varying this ratio in the range from 10 to 100 mmol/dm^3. Within these experiments, the reaction temperature was kept constant at 90 °C, and chemical modeling was performed. Fig. 2 shows that the curves of $Ca(OH)_2$ and $Mg(OH)_2$, like the effect of reaction temperature, were shifted to the left by increasing initial amount, whereas the $Mn(OH)_2$ curve became wider. The precipitation changes of Ca, Mg, $Mn(OH)_2$ at various conditions of initial amount in Fig. 2 are involved mainly in the solubility of hydroxide. This suggests that the increase of initial amount suppresses the solubility of each precipitated hydroxide; the explanation for Mg behavior (as well as Ca and Mn) concerns the two chemical reactions given by (c) $MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$ and $Mg^{2+} + 2OH^- \rightarrow$ (d) $Mg(OH)_2$ wherein solubility of (d) decreased in response to a raised Mg ion concentration by the increase of (c) with increasing initial amount. Moreover, it leads to a decrease in pH of solution; in other words, the initial amount does not affect the yield of precipitation directly. However the precipitation data presented in Fig. 2 as well as Figs. 1 and 3 suggest the benefit of applying a two-stage process for lithium recovery, as shown in Fig. 4 which is discussed in detail below.

3.1.3. Multiple components of Ca, Mg, and Mn in $CaCl_2$-$MgCl_2$-$MnCl_2$-NaOH-H_2O solutions

The precipitation behavior of $Ca(OH)_2$, $Mg(OH)_2$, and $Mn(OH)_2$ in $CaCl_2$-$MgCl_2$-$MnCl_2$-NaOH-H_2O solutions as a function of pH at 90 °C was investigated to predict the conditions for selective precipitation of Ca, Mg, and Mn. The initial amount was kept constant at 10 mmol/dm^3. The chemical modeling fitted by OLI-Systems® software is shown in Fig. 3(a) and was in good agreement with the experimental values. This result shows that the Ca, Mg, and $Mn(OH)_2$ precipitate was more than 95% in the pH range from 11.5 to 12.5. However, according to Figs. 1 and 2, it is possible to change the pH range for maximum yield by changing the reaction temperature and the C/S, as shown in Fig. 3(b) and (c).

3.2. Study of lithium recovery from seawater via two-stage precipitation process

Among adsorbents used in the adsorption process for lithium recovery from seawater, spinel-type hydrous manganese oxides are