Fractional crystallization for extracting lithium from Cha'erhan tail brine

Weiping Liu *, Hui Xu, Xichang Shi, Xiyun Yang

School of Metallurgy and Environment, Central South University, Changsha 410083, China

ARTICLE INFO

ABSTRACT

According to the solubility isotherms of the ternary system ($LiCl + NH_4Cl + H_2O$), fractional crystallization including primary crystallization and secondary crystallization, was designed to remove the maximum amount of NH_4^+ from Cha'erhan tail brine and raise the concentration of Li^+. The particle size and surface topography during fractional crystallization were studied by XRD and SEM techniques. Then, sodium hydroxide was used for the removal of magnesium, and high purity sodium carbonate was obtained by the method of carbonation from Cha'erhan tail brine.

1. Introduction

Lithium has been used in many industries, such as the manufacturing of glass, ceramics, rubbers, pharmaceuticals, and the production of lithium-ion batteries (Vikström et al., 2013; Xu et al., 2011). As the base material of lithium salts, other industrial lithium products are downstream products of lithium carbonate (Lee et al., 2013; Liao et al., 2015). Granite-pegmatite deposits, salt lake brine, seawater, and hot springs are the primary lithium resources worldwide (Shi et al., 2011). As the requirement for lithium and its compounds continue to increase in various fields, one area of growing concern is extracting lithium from brine as lithium carbonate (Xu et al., 2009).

In this regard, extraction of lithium from Cha'erhan salt lake brine (Qinghai, China) is a demanding program at present and in future. The ratio of lithium to magnesium is a crucial factor in recovery of lithium from brines. The higher concentration of magnesium in the brine, the slower evaporation rate and lower lithium yield are obtained. Therefore, an economical method to separate lithium and magnesium in the Cha'erhan salt lake brine with such a low mass Li^+/Mg^{2+} ratio of 0.025–0.100 is urgently needed.

The main methods of extracting lithium from low mass ratio of Li^+/Mg^{2+} brine are solvent extraction, ion exchange, precipitation and calcinations-leaching (Fu and Hui, 2010; Petersková et al., 2012), etc. Solvent extraction and ion exchange methods depend on the high efficient, high reliable and environmental friendly ion exchangers and extractants,

which are limited by the cost. While the precipitation and calcinations-leaching methods encounter the disadvantages of complex schedules and high energy consumption (Sun et al., 2007). Among the separation methods proposed is the method suggested by Xu et al. (2007, 2009), in which sulfuric acid process removed the boron, then NH_3 gas and NH_4HCO_3 were added respectively in order to precipitate about 98% of Mg^{2+} as $Mg(OH)_2$ and $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$ respectively. Finally the tail brine was obtained, and the NH_3 gas was reproduced by reacting CaO with NH_4Cl at high temperatures thereby guaranteeing its economy. It is well known that the brine system gradually converts from $MgCl_2 + LiCl + H_2O$ into $MgCl_2 + LiCl + NH_4Cl + H_2O$, and finally into $LiCl + NH_4Cl + H_2O$ as tail brine in the process of adding ammonia gas and ammonium bicarbonate to precipitate Mg^{2+}. However, the details about utilization of the $LiCl + NH_4Cl + H_2O$ tail brine are still unknown and are the subject of this paper, which includes NH_4^+ removal and Li^+ precipitation.

Meanwhile, salt-water phase diagram is of importance for the separation of certain component from solution. The phase diagram has been used in the inorganic salt, fertilizer and soda industries (Kbir-Ariguib et al., 2001), etc. Therefore, the solubility isotherms of the ternary system ($LiCl + NH_4Cl + H_2O$) at 298.15 K (Ouyang et al., 2011) is used for the utilization of Cha'erhan tail brine in this study.
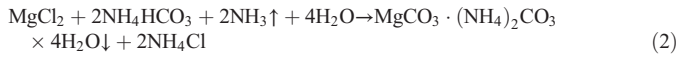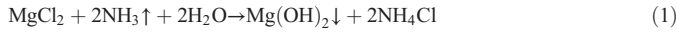
In this regard, based on the solubility isotherms of the ternary system ($LiCl + NH_4Cl + H_2O$), fractional crystallization including primary and secondary crystallizations has been designed and conducted at 298.15 K to remove the component of NH_4^+ and raise the concentration of Li^+. Meanwhile, the principles of particle size and surface topography during fractional crystallization were studied. Finally, NaOH is chosen to raise the mass ratio of Li^+/Mg^{2+}, and Na_2CO_3 is used as precipitant for the final product of lithium carbonate.

---

2. Material and methods

Sodium and potassium from Cha'erhan salt lake brine were removed by solar ponds production at first. The composition of brine after the removal of sodium and potassium is listed as: B_2O_3 2– 4%, Mg^{2+} 80– 120 g/l, Li^+ 3– 8 g/l (Xu et al., 2007). The boron was removed by sulfuric acid, and magnesium was removed by adding NH_3 gas and NH_4HCO_3 respectively. The main chemical equations are below (Xu et al., 2009).

$$MgCl_2 + 2NH_3\uparrow + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2NH_4Cl \tag{1}$$

$$MgCl_2 + 2NH_4HCO_3 + 2NH_3\uparrow + 4H_2O \rightarrow MgCO_3 \cdot (NH_4)_2CO_3 \\ \times 4H_2O\downarrow + 2NH_4Cl \tag{2}$$

After the removal of sodium, potassium, boron and magnesium, the main composition of the Cha'erhan tail brine is listed as Li^+ 4.5 g/l, Mg^{2+} 1.9 g/l, NH_4^+ 81.8 g/l, Cl^- 189.3 g/l. Thus the Cha'erhan tail brine can be treated as $NH_4Cl + LiCl + H_2O$ ternary system due to small amount of Mg^{2+} ion. According to the phase diagram of the $NH_4Cl + LiCl + H_2O$ system at 298.15 K in Fig. 1 (Ouyang et al., 2011), fractional crystallization including primary crystallization and secondary crystallization in the NH_4Cl crystallization branch of the phase diagram, was designed to remove the component of NH_4^+ and raise the concentration of Li^+.

The Cha'erhan tail brine was designated as point "a (■)" in Fig. 1. During the primary crystallization, 65 wt% of brine was evaporated and the brine can be concentrated to point "b" $[w_{NH_4Cl}/(w_{NH_4Cl} + w_{LiCl}) = 0.900]$ from point "a", then NH_4Cl was crystallized and the brine reached point "c" $[w_{NH_4Cl}/(w_{NH_4Cl} + w_{LiCl}) = 0.425]$. After that, secondary crystallization followed. In order to avoid the formation of $LiCl \cdot H_2O$ along with NH_4Cl, the salt composition in the brine should be controlled to $w_{NH_4Cl}/(w_{NH_4Cl} + w_{LiCl}) > 0.13725$ at 298.15 K (Ouyang et al., 2011). Therefore, 36 wt% of brine was evaporated and the brine reached point "d" $[w_{NH_4Cl}/(w_{NH_4Cl} + w_{LiCl}) = 0.425]$, then point "e" $[w_{NH_4Cl}/(w_{NH_4Cl} + w_{LiCl}) = 0.13725]$ after the crystallization of NH_4Cl. Thus, it can be seen that $w_{NH_4Cl}/(w_{NH_4Cl} + w_{LiCl})$ can theoretically decrease from 0.900 to 0.13725 through the fractional crystallization process.

Each evaporation experiment consumed 100 ml brine. The experiment was conducted in a glass evaporating dish, which was heated by a resistance furnace. An exhaust fan was placed to supply a discontinuous air draft, which accelerated the rate of evaporation. Newly samples were obtained from different evaporation capacities, and then were chemically analyzed. After the filtration, the solid and liquid phases were separated, and the relevant parameters were determined. Liquids and solids collected from primary crystallization are designated as L1, L2, L3, L4, L5 and S1, S2, S3, S4, S5 respectively. Then, L5 was chosen as raw material for the secondary crystallization. The liquid and solid collected from secondary crystallization were named as L6 and S6 separately.

The concentration of NH_4^+ was determined by the method of distillation combined with acid-base titration (Haitang et al., 2012). The concentration of Mg^{2+} was determined by titrating the Mg^{2+} with EDTA. The total concentration of $MgCl_2$, $LiCl$, and NH_4Cl in the system was determined by precipitating Cl^- ions with $AgNO_3$ (Kolthoff et al., 1969). The difference between the total amount of Cl^- and the sum of NH_4^+ and Mg^{2+} gives the concentration of Li^+. Evaporation capacity means the volume of water which evaporated in the evaporating experiment.

3. Results and discussions

3.1. Fractional crystallizations

Based on the solubility isotherms of the $(LiCl + NH_4Cl + H_2O)$ ternary system and the "level rule", 70 g water from 100 ml brine (L1) was evaporated during the primary crystallization to reach point "b", and then 40 g water from 100 ml brine (L5) in the secondary crystallization to reach point "d". In order to have a preliminary evaluation of the filtration performance of the crystallized solids, several samples were collected at different evaporation capacity during the fractional crystallization in order to observe the principles of particle size and surface topography.

3.1.1. Primary crystallization

The samples were collected at different evaporation capacities of 30, 40, 50, 60, 70 g water per 100 ml brine. The chemical composition of liquids and solids is shown in Figs. 2 and 3.

As shown in Fig. 2, it is obvious that the concentration of Li^+ increases from 4.5 to 30.50 g/l as the increasing of the evaporation capacity. However, the mass ratio of Li^+/Mg^{2+} fluctuates around 2, further magnesium removal is needed to increase the mass ratio of Li^+/Mg^{2+}. Meanwhile, the concentration of NH_4^+ decreases from 85.66 g/l to 57.30 g/l with the evaporation capacity of 60 g, then few variables is observed while the evaporation capacity increases to 70 g. The results above indicate that the primary crystallization has removed the theoretical maximum amount of NH_4^+ from the tail brine according to the phase diagram of $LiCl + NH_4Cl + H_2O$. In order to further remove NH_4^+, secondary crystallization is needed.
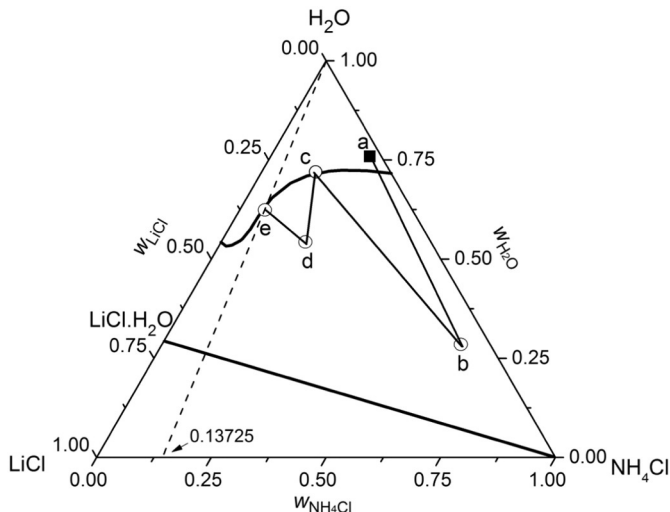

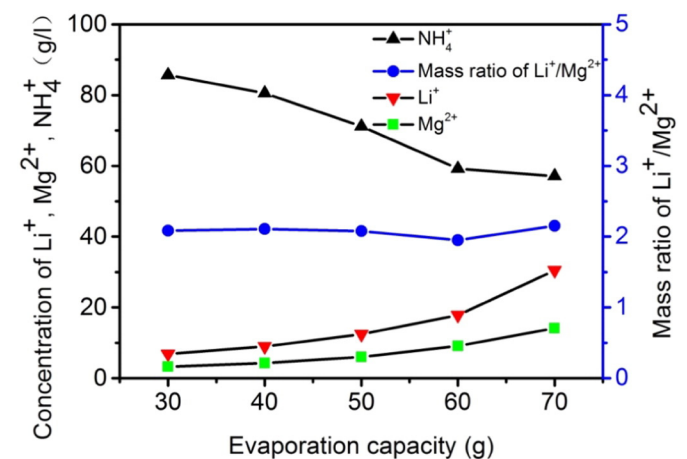Fig. 1. Phase diagram of the system $NH_4Cl + LiCl + H_2O$ at 298.15 K (Ouyang et al., 2011).

Fig. 2. Relationship between concentration of Li^+, Mg^{2+}, NH_4^+, mass ratio of Li^+/Mg^{2+} and evaporation capacity.