Fractional Crystallization for Extracting Lithium from Cha'erhan Tail Brine

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Abstract: According to the solubility isotherms of the ternary system (LiCl+NH₄Cl+H₂O), fractional crystallization including primary crystallization and secondary crystallization, was designed to remove the maximum amount of NH₄⁺ 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.

Keywords: fractional crystallization; extracting; lithium; brine; phase diagram; Cha'erhan

1. Introduction

Lithium has been used in many industries, such as the manufacturing of glass,

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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 $\text{Li}^+/\text{Mg}^{2+}$ ratio of 0.025-0.100 is urgently needed.

The main methods of extracting lithium from low mass ratio of $\text{Li}^+/\text{Mg}^{2+}$ 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 (Xu et al., 2009, 2007), 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 $\text{Mg}(\text{OH})_2$ and $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ 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 $\text{MgCl}_2 + \text{LiCl} + \text{H}_2\text{O}$ into $\text{MgCl}_2 + \text{LiCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$, and finally into $\text{LiCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$ as tail brine in the process of adding ammonia gas and ammonium bicarbonate to precipitate Mg^{2+} . However, the details about utilization of the $\text{LiCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$ 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 ($\text{LiCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$) 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 ($\text{LiCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$), fractional crystallization including primary and secondary

crystallizations has been designed and conducted at 298.15K 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 $\text{Li}^+/\text{Mg}^{2+}$, 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).

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 $\text{NH}_4\text{Cl}+\text{LiCl}+\text{H}_2\text{O}$ ternary system due to small amount of Mg^{2+} ion. According to the phase diagram of the $\text{NH}_4\text{Cl}+\text{LiCl}+\text{H}_2\text{O}$ 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

Fig. 1. Phase diagram of the system $\text{NH}_4\text{Cl}+\text{LiCl}+\text{H}_2\text{O}$ at 298.15 K (Ouyang et al., 2011).

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" [$w_{\text{NH}_4\text{Cl}}/(w_{\text{NH}_4\text{Cl}}+w_{\text{LiCl}}) = 0.900$] from point "a", then NH_4Cl was crystallized and the brine reached point "c" [$w_{\text{NH}_4\text{Cl}}/(w_{\text{NH}_4\text{Cl}}+w_{\text{LiCl}}) = 0.425$]. After that, secondary crystallization followed. In order to avoid the formation of $\text{LiCl}\cdot\text{H}_2\text{O}$ along with NH_4Cl , the salt composition in the brine should be controlled to $w_{\text{NH}_4\text{Cl}}/(w_{\text{NH}_4\text{Cl}}+w_{\text{LiCl}}) > 0.13725$ at 298.15 K (Ouyang et al., 2011). Therefore, 36 wt % of brine was evaporated and the brine reached point "d" [$w_{\text{NH}_4\text{Cl}}/(w_{\text{NH}_4\text{Cl}}+w_{\text{LiCl}})$]

=0.425], then point "e" [$w_{\text{NH}_4\text{Cl}}/(w_{\text{NH}_4\text{Cl}}+w_{\text{LiCl}}) = 0.13725$] after the crystallization of NH_4Cl . Thus, it can be seen that $w_{\text{NH}_4\text{Cl}}/(w_{\text{NH}_4\text{Cl}}+w_{\text{LiCl}})$ 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+NH₄Cl+H₂O) ternary system and the "level rule", 70g water from 100 ml brine (L1) was evaporated during the primary crystallization to reach point "b", and then 40g water from 100ml 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, 70g water per 100 ml brine. The chemical composition of liquids and solids are shown in Fig. 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⁺/Mg²⁺ fluctuates around 2, further magnesium removal is needed to increase the mass ratio of Li⁺/Mg²⁺. Meanwhile, the concentration of NH₄⁺ decreases from

85.66 g/l to 57.30 g/l with the evaporation capacity of 60g, then few variables is observed while the evaporation capacity increases to 70g. The results above indicate that the primary crystallization has removed the theoretical maximum amount of NH_4^+ from the tail brine according the phase diagram of $\text{LiCl}+\text{NH}_4\text{Cl}+\text{H}_2\text{O}$. In order to further remove NH_4^+ , secondary crystallization is needed.

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

Fig. 3. Relationship between mass percent of Li^+ , Mg^{2+} , NH_4^+ and evaporation capacity.

The mass percentages of Li^+ and Mg^{2+} in solids increase steadily, with the rate of less than 1% and 0.5% separately as shown in Fig. 3. The mass percentage of NH_4^+ during primary crystallization is around 66.3%, which is the theoretical mass percentage of $\text{NH}_4^+/\text{NH}_4\text{Cl}$. Together with the XRD results of "S1", "S3" and "S5" as shown in Fig. 4, these results confirm that NH_4Cl is the only solid phase and no other phases existed. The results above are consistent with the solubility isotherms of the ternary system ($\text{LiCl}+\text{NH}_4\text{Cl}+\text{H}_2\text{O}$), which indicates that the route of fractional crystallization is in the NH_4Cl crystallization branch.

Fig. 4 XRD results.

3.1.2 Secondary crystallization

It is noted that the secondary crystallization increased the concentration of Li^+ up to the maximal concentration of 38.82 g/l, avoiding the formation of $\text{LiCl}\cdot\text{H}_2\text{O}$ at the

same time as "S6" confirmed in Fig. 4. The concentration of Mg^{2+} also increased to 18.83 g/l, magnesium removal procedure is thus followed to increase the mass ratio of $\text{Li}^+/\text{Mg}^{2+}$.

Fig. 5 SEM patterns of the solids.

Fig. 5 shows that the particle size of sheet-shape NH_4Cl increases with the evaporation capacity during primary crystallization, and its particle size is in the range of 50-500 μm . During the secondary crystallization, the particle size is sharply decreased to 50-150 μm , which is caused by the higher concentration of the tail brine in secondary crystallization comparing with the case in primary crystallization.

Based on the ammonia chloride particle size of larger than 50 μm , it is expected that low moisture content, high filtration speed of ammonia chloride can be achieved (Xu et al., 2005). The particle size and surface tomography is associated with the filtration performance. Further systematic examinations concerning about the surface tomography, particle size and filtration performance during the fractional crystallization are necessary, which parameters include evaporation intensity, temperature, and the evaporation method, etc.

3.2 Removal of Mg^{2+}

The main reagents for the precipitation of magnesium are ammonia gas, calcium hydroxide and sodium hydroxide (Xu et al., 2009). Considering the features of high purity and strong alkaline, sodium hydroxide is chosen to remove magnesium. The reactions are shown as equations (3-4). The optimum factors are followed: sodium hydroxide excessive factor 1.5; 25 $^{\circ}\text{C}$; reaction time 15 min; aging time 45 min; NaCl addition (50% of this reaction output); $\text{Mg}(\text{OH})_2$ addition (50% of this reaction output).

Mg^{2+} precipitated as $\text{Mg}(\text{OH})_2$ with the purity of 99.50% and Li^+ remained in the solution due to the huge difference between solubility of $\text{Mg}(\text{OH})_2$ (0.0009g/100g; 18°C) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (12.8g/100g; 20°C) (Yao et al., 1983). The concentration of Li^+ raised a little from 38.82 to 39.52 g/l, and the mass ratio of $\text{Li}^+/\text{Mg}^{2+}$ increased from 2.06 to 34.07 dramatically. It should be noted that NH_4Cl and $\text{NH}_3\cdot\text{H}_2\text{O}$ coexisted and formed a buffer system, especially at the end of the magnesium removal process as shown in equation (4). Therefore, the pH value of the solution is in a stable area of less than 12, which is the preferred pH for the precipitation of Mg^{2+} (Xu et al., 2009). Thus the removal efficiency of Mg^{2+} is limited to 90.76%.

3.3 Precipitation of Li^+ by Na_2CO_3

Lithium carbonate is usually prepared by adding sodium carbonate into lithium chloride solution. Suitable factors are below: sodium carbonate excessive factor 1.5; 90 °C; reaction time 2 h; Li_2CO_3 addition (50% of the reaction output); 250 r/min.

The element analysis showed that the precipitation efficiency of Li^+ reaches 96.10%, and only 1.10 g/l of Li^+ was left in the tail brine. However, the purity of lithium carbonate only reached 98.20% due to the limited removal efficiency of Mg^{2+} . Following purification of Li_2CO_3 is needed. The slurry was then leached with carbon

dioxide gas and the resulting bicarbonate solution was heated to prepare lithium carbonate as shown in equations (6-7) (Jandová et al., 2010). According to the ICP and AAS measurements results in Table 1, the purity of lithium carbonate reached 99.70%, which is comparable with the lithium carbonate of 99.55% prepared from Uyuni salar brine, Bolivia (An et al., 2012). The XRD measurement confirms that lithium carbonate is the main phase and no other phases coexisted.

Table 1. Purity of Li_2CO_3 and content of major impurities.

Purity of	Content of major impurities, %					
Li_2CO_3 , %	Mg	Na	K	Al	Si	P
99.70	0.04	0.04	0.038	0.0016	0.025	0.04

However, the origins of the impurities in lithium carbonate, the distribution and the specific existing forms of the impurities associated with the fractional crystallization, magnesium removal and lithium carbonation procedures are still unknown. In order to have a better impurity control in the production of lithium carbonate, a systematic examination of the impurities is needed.

4. Conclusions

Based on the solubility isotherms of the ternary system ($\text{LiCl}+\text{NH}_4\text{Cl}+\text{H}_2\text{O}$), fractional crystallization including primary crystallization and secondary crystallization was designed to remove the maximum amount of NH_4^+ . Then magnesium removal and lithium precipitation procedures were followed to obtain the high purity lithium carbonate. The preliminary research indicates that the method discussed above is a promising way for the utilization of Cha'erhan salt lake tail brine. The pilot test is needed.

Conclusions at this time include the following points:

1. The fractional crystallization including primary crystallization and secondary crystallization raised the Li^+ concentration of Cha'erhan tail brine from 4.5 g/l up to the maximum concentration of 38.82 g/l, and the maximum amount of NH_4^+ was removed at the same time.
2. The particle size of the sheet-shape NH_4Cl is in the range of 50-500 μm for the primary crystallization, and 50-150 μm for the secondary crystallization.
3. The mass ratio of $\text{Li}^+/\text{Mg}^{2+}$ increases dramatically from 2.06 to 34.07 after the removal of magnesium, and high purity of 99.70% lithium carbonate is obtained finally.

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5. References

- An, J.W., Kang, D.J., Tran, K.T., Kim, M.J., Lim, T., Tran, T., 2012. Recovery of lithium from Uyuni salar brine. *Hydrometallurgy* 117–118, 64–70. doi:10.1016/j.hydromet.2012.02.008
- Fu, Y., Hui, Z., 2010. Research situation of separating magnesium and lithium from high Mg/Li ratio salt lake brine. *Multipurp. Util. Miner. Resour.* 2, 10.
- Haitang, Y., Dewen, Z., Yan, Y., 2012. Determination of NH_4^+ and NO_3^- in salt-water system by distillation-acid-base titration. *Metall. Anal.* 32, 23–28.
- Jandová, J., Dvořák, P., Hong, N.V., 2010. Processing of zinnwaldite waste to obtain Li_2CO_3 . *Hydrometallurgy* 103, 12–18.
- Kbir-Ariguib, N., Chehimi, D.B.H., Zayani, L., 2001. Treatment of Tunisian salt lakes using solubility phase diagrams. *Pure Appl. Chem.* 73, 761–770.
- Kolthoff, I.M., Sandell, E.B., Meehan, E.J., Bruckenstein, S., 1969. Quantitative chemical analysis. Macmillan London.
- Lee, J., Yu, S.H., Kim, C., Sung, Y.E., Yoon, J., 2013. Highly selective lithium recovery from brine using a $\lambda\text{-MnO}_2\text{-Ag}$ battery. *Phys Chem Chem Phys* 15, 7690–7695. doi:10.1039/c3cp50919b
- Liao, H., Xu, H., Li, G., Cheng, J., Liu, W., 2015. Study on preparation of carbonate lithium from magnesium hydroxide waste of lithium extraction process by nanofiltration. *Mater. Rev.* 29, 90–94.

- Ouyang, H., Zeng, D., Zhou, H., Han, H., Yao, Y., 2011. Solubility of the ternary system $\text{LiCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$. J. Chem. Eng. Data 56, 1096–1104. doi:10.1021/je101056t
- Petersková, M., Valderrama, C., Gibert, O., Cortina, J.L., 2012. Extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis concentrate using selective sorbents. Desalination 286, 316–323. doi:10.1016/j.desal.2011.11.042
- Shi, X., Zhou, D., Zhang, Z., Yu, L., Xu, H., Chen, B., Yang, X., 2011. Synthesis and properties of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and its adsorption application. Hydrometallurgy 110, 99–106. doi:10.1016/j.hydromet.2011.09.004
- Sun, X., Chen, B., Xu, H., Shi, X., 2007. Extraction of lithium from bittern. J. Cent. South Univ. 38, 262–266.
- Vikström, H., Davidsson, S., Höök, M., 2013. Lithium availability and future production outlooks. Appl. Energy 110, 252–266.
- Xu, H., Li, X., Chen, B., Shi, X., Liu, R., Ma, Y., Deng, X., 2005. Method of preparing high purity magnesium sand using salt lake bischofite as raw material. CN1618998 A.
- Xu, H., Liu, W., Su, Y., Shi, X., Yang, X., 2011. Study on synthesis of $\text{Li}_{1-x}\text{Cr}_x\text{FePO}_4$ by microwave processing. Mater. Rev. 25, 150–152.
- Xu, H., Mao, X., Li, Z., Shi, X., Pang, Q., Chen, B., Yang, X., Wang, H., 2007. Method for combined extracting boron, magnesium and lithium from salt lake bittern. CN100528753 C.
- Xu, H., Xu, L., Chen, B., Shi, X., Yang, X., 2009. Separating technique for magnesium and lithium from high Mg/Li ratio salt lake brine. J. Cent. South Univ. 40, 36–40.
- Yao, Y., Xie, T., Gao, Y., 1983. Handbook of physical chemistry. Shanghai scientific & technical publishers.