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Short Communication

Manufacture of sodium-free lithium chloride from salt lake brine

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ABSTRACT

Process assessment experiment was conducted to investigate the applicability of integration technology (CCI, concentration, cooling and ion exchange) to manufacture sodium-free lithium chloride from salt lake brine. The preliminary separation process of sodium from brine, using evaporating concentration by adding surfactant, showed the amount of sodium in brine decreases to below 0.187%. Then, brine was further cooling separation process which was characterized in that the ammonia is added in order to decrease the solubility of NaCl. The purification of lithium chloride from cooling brine was then conducted with a novel separation process which was designed by a novel ion exchange method using inorganic ion-exchanger $Li_{1.4}Cr_{0.4}Ti_{1.6}(PO_4)_3$. The total yield of LiCl with the present purification process was 86.16%, and the sodium concentration in the supernatant is 0.0005 wt.%.

1. Introduction

Salt lake resources are very abundant in China, and the lithium in the brine is quite famous in the world [1]. But now the exploitation of salt lake resources in China is just at the elementary level. At present, the demands for lithium chloride, especially the sodium-free lithium chloride, are increasing rapidly. Lithium chloride is all just an industrial raw material, from which lithium compounds and in particular metallic lithium are produced. To make additional processing of the lithium chloride more economic and efficient, it is quite necessary to give the raw material as pure as possible. Sodium in lithium metal is very harmful, even if a few of sodium (about 0.01%) would make it highly reactive and much different in properties than purity lithium metal. So as the raw material of lithium chloride, it is necessary for low content of sodium [2–5].

Lithium naturally coexists with many other minerals such as sodium, calcium and magnesium. At present, the commonly used separation methods including the solvent extraction, salting out, ion-exchange, coprecipitation method, nanofiltration, etc. There has no any single technique that will meet all requirements; so we must design a series of interrelated techniques according to the composition of brine [6–10].

It is well known that solutions containing lithium chloride, which is contaminated with sodium chloride, can be purified by evaporating the solution, cooling the evaporated solution and separating the crystallized sodium chloride [11]. This process becomes feasible in that sodium chloride is under a lower solubility in water than lithium chloride. When alkali chlorides are present in an aqueous solution, the solubility of the sodium chloride is reduced by the presence of the lithium chloride; sodium chloride is pushed out of the solution by the lithium chloride, so to speak, and will crystallize out, where this effect becomes effective in particular when the contaminated solution is cooled to temperatures <0 °C.

Natrium superionic conductor (NASICON) ceramics present interesting sensitive and selective properties against alkaline cations due to their structure. In the ion-covalent structure, Li^+ move from one site to another passing through bottlenecks defined by the anionic skeleton. NASICON materials are especially good candidates to determine alkaline ion concentrations in solution or to separate monovalent cations from a mixture of multivalent ions [12,13,9,14].

The purpose of the present work was to investigate the applicability of integration technology (CCI, concentration, cooling and ion exchange) for recovering sodium-free lithium chloride from lithium-containing brine, based on process assessment experiments and technical comparison.

2. Experimental

2.1. Materials and chemicals

The composition of brine used throughout this work was drawn from salt lake brines and supplied by the Qinghai Lithium Co. Ltd., China. The chemical analyses of the brain are shown in Table 1. All the chemicals *Viz.*, dodecyl benzene sulfonic acid sodium salt (LAS),

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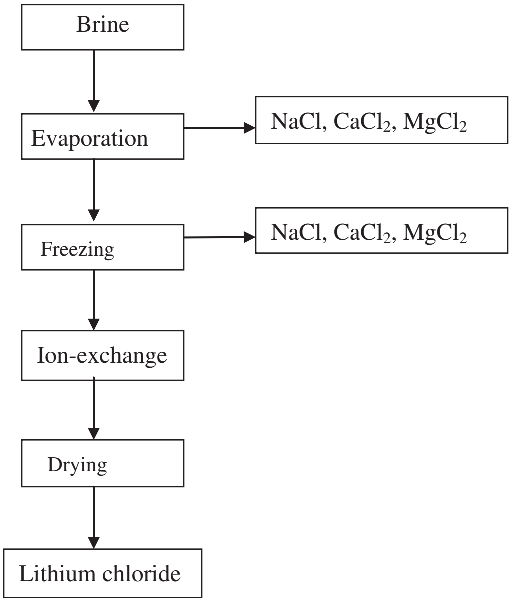

Fig. 1. Purification processes of lithium from brine.

p-acetamidobenzene sulfonyl chloride (ASC), ammonia, LiOH and NaOH used in the experiment are of analytical grade and purchased from the Shanghai Chemical Reagent Corporation. The stock LiCl, NaCl, $CaCl_2$ and $MgCl_2$ solution was used for calibration in flame atomic absorption spectroscopy (FAAS) analysis. The ion exchange $Li_{1.4}Cr_{0.4}Ti_{1.6}(PO_4)_3$ (LCTP) was prepared from a mixture of Li_2CO_3, TiO_2, Cr_2O_3, and $NH_4H_2PO_4$ as described in the previous articles [15].

2.2. Experimental procedure

The purification process for the separation of sodium, calcium, and magnesium was constructed, based on the experimental results and the subsequent data analysis. The process flow is shown in Fig. 1. The method is useful to prepare lithium compounds with high value and the comprehensive utilization of salt lake lithium resource.

Batch experiments were conducted using a certain amount of ion exchanger added to the cooling lithium chloride brine. The mixture was shaken constantly at a speed of 200 RPM. Aliquots were removed at predetermined time intervals within a period of 200 min. The solutions were centrifuged at a speed 3500 RPM for 5 min and Na(I) ion concentration in the supernatant measured by FAAS.

The effect of varying ion exchanger mass while maintaining the concentration constant was studied as follows: 1.00, 1.05 and 1.10 g portions of the ion exchanger were placed in 100 g 39.20% (w/w) lithium chloride brine at 60 ± 1 °C. The mixture was shaken constantly at a speed of 200 RPM. After 200 min, the solutions were centrifuged at a speed 3500 RPM for 5 min and Na(I) ion concentration in the supernatant measured by FAAS.

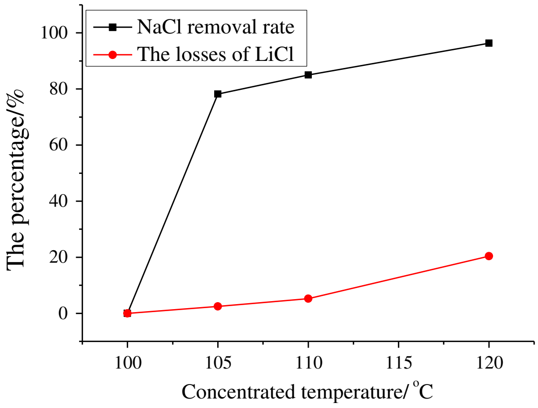

Fig. 2. Effect of temperature on the NaCl removal rate and the loss of LiCl.

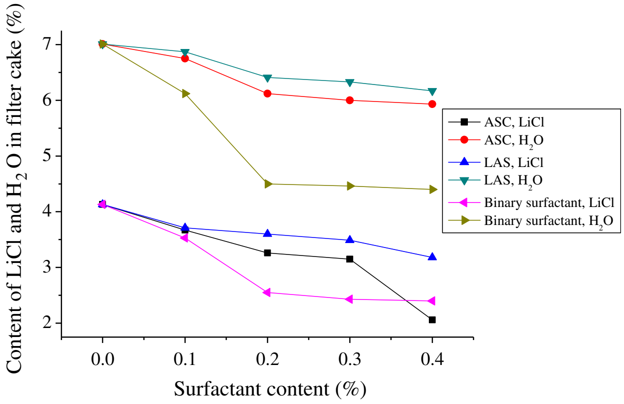

Fig. 3. Effect of surfactant on the loss of LiCl and the cake moisture.

2.3. Methods of analysis

FAAS was used for analysis of Na^+, Li^+, Ca^{2+}, Mg^{2+}, Australia, GBC-932 AAS. Magnetic stirrer model DF-101B (Yuying·Shanghai, voltage adjusting and temperature controlling) was used in agitating the samples at the required speeds while the centrifuge model Xiangzhi TDZ5-WS series was used for dividing the residue from the solution.

3. Results and discussion

3.1. Concentration and evaporation process

During the process of extracting lithium chloride from brine, how to get rid of sodium chloride and reduce the loss of lithium chloride by evaporation and crystallization is one of the fundamental problems. In addition, sodium chloride easily scales on the bottom of the evaporator, which makes the operation of filtration

Table 1
Metal ion concentrations in the solution in each step of the purification.

	Li^+ (wt.%)	Na^+ (wt.%)	Ca^{2+} (wt.%)	Mg^{2+} (wt.%)	Na/LiCl (%)	LiCl (wt.%)	Density of brine (g/mL)
Feedstock	0.8534	3.129	0.0053	0.0931	57.99	5.38	1.085
First concentrated brine	3.221	0.3062	0.8086	0.6228	0.1552	2.011	1.158
Second concentrated brine	7.496	0.0725	1.110	0.8598	0.0174	45.07	1.286