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Extraction of lithium from salt lake brine containing boron using multistage centrifuge extractors

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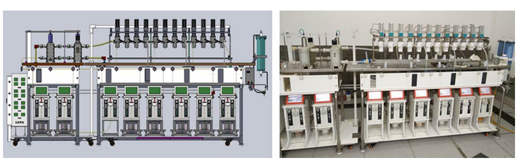
GRAPHICAL ABSTRACT



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ABSTRACT

Lithium extraction process from salt lake brine containing H_3BO_3 was investigated in this paper. The extraction, scrubbing, stripping and regeneration processes were studied respectively, using *N*, *N*-bi-(2-ethylhexyl) acetamide (N523) and tri-butyl phosphate (TBP) as the extractant, kerosene as diluent and $FeCl_3$ as co-extractant. H_3BO_3 present in the brine could be extracted by TBP in the extraction stage. The presence of H_3BO_3 had no significant effect on lithium extraction efficiency and separation effect between lithium and magnesium. The main portion of the extracted H_3BO_3 could be scrubbed in the scrubbing stage, magnesium could be nearly scrubbed completely. The whole extraction process experiment and magnified experiment were conducted on separating funnels and centrifugal extractors, respectively, and no third phase appeared. The lithium extraction rate reached 96%. The Mg/Li mass ratio changed from 48 in salt lake brine to 0.0015 in the stripping liquor, meanwhile, H_3BO_3/Li mass ratio changed from 5.6 to 0.018. The stripping liquors contained 28 g/L Li^+ with small amounts of H_3BO_3, and other impurity ions. This study indicated that the presence of H_3BO_3 in salt lake brine had no significant influence on lithium extraction and quality of stripping liquors. Furthermore, it was shown that centrifugal extractors were effective in the lithium extraction process.

1. Introduction

Lithium is an important strategic element, which is widely applied in chemical industry, including manufacture of glass and ceramics, pharmacy, special alloy, catalyst, refrigerant etc. With the rapid development of lithium ion battery, energy storage electronic and controlled nuclear fusion fuel, the demand of lithium has been accelerated under the energy shortage condition [1–4]. Brine and high-grade lithium ores are the present sources for all lithium production, and the salt lake brine is the biggest resource for lithium occurrence [5,6]. Lithium is richly reserved in the brine of Qinghai Qaidam basin salt lakes with a total of 1.52×10^6 t in LiCl, which accounts for about 80% of the total brine lithium resource found in China [7].

The concomitant boric acid, alkali and alkaline earth metal ions together with lithium in salt lake brine make the separation of lithium difficult. Solvent extraction is considered one of the most powerful

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techniques for lithium separation from salt lake brine, which possesses advantages of high selectivity, attractive economics, environment friendliness and possibilities of operations in continuous mode [8]. Recent researches on lithium recovery from brine focused on separation lithium from magnesium, and other concomitant metal ions. Xiang et al. reported that TBP/$FeCl_3$ in methyl isobutyl ketone (MIBK) was an effective extraction system for lithium recovery from salt lake brine with high Mg/Li ratio. The overall lithium recovery was higher than 98% and the Mg/Li molar ratio changed from 94.8 in salt lake brine to 0.03 in the stripping solution. Extensive studies were made of the extraction mechanism. It was found that the sequence of the capabilities of various ions to bind with TBP + $FeCl_3$ was $H^+ > Li^+ > \ > Mg^{2+} > Na^+$ [9–14]. Ionic liquid containing organic phosphorous were used as extractants by Shi et al. to extract lithium from salt lake brine with high Mg/Li ratio, which showed considerable lithium extraction rate and excellent separation efficacy between lithium and magnesium [15–17]. In our previous works, amine was confirmed to be a valuable extractant for industry application. An eight-stage extraction process including extraction, scrubbing, stripping and regeneration was conducted. Using N523 and TBP as extractants and $FeCl_3$ as co-extractant, the extraction rate of lithium reached 96% with low impurity in stripping liquor [18]. The extraction mechanism of the systems involved amine was researched also, including co-extraction effect, salting-out effect, co-existing ions effect, thermodynamics and kinetics [19–24].

The mechanism of lithium extraction process involved $FeCl_3$ could be summarized as follows [9,22,23].

$$mM^{\frac{1}{m}+}_{(aq)} + Fe^{3+}_{(aq)} + 4Cl^{-}_{(aq)} \leftrightarrow M_mFeCl_{4(aq)}$$

$$M_mFeCl_{4(aq)} + nS_{(org)} \leftrightarrow M_mFeCl_4\bullet nS_{(org)}$$

Fe^{3+} can coordinate with Cl^- forming $FeCl_4^-$ anionic complex in the solution with relatively higher concentration of Cl^-, and metal cations in salt lake brine, such as Li^+, Mg^{2+}, Na^+, K^+, combine with $FeCl_4^-$ to balance charge and form M_mFeCl_4 species. When the salt lake brine containing $LiFeCl_4$ species contacts specific extractants (expressed as **S**), the $M_mFeCl_4\cdot nS$ species formed through coordination and then transfer to organic phase.

The diagram shown in Fig. 1 can help us understand the principle of the whole extraction cycle. S refers to extractants and M refers to Na^+, K^+, Mg^{2+}, Ca^{2+} and other coexisting cations. Cation exchange plays a dominant role in the extraction, scrubbing and stripping processes, and the acid-base neutralization facilitates the regeneration process. In essence, the overall reaction in the extraction cycle is an acid-base neutralization. The stability of the co-extractant $FeCl_3$ loaded on the organic phase in the whole extraction process is the prerequisite of a satisfactory result, which requires > 6 mol/L concentration of Cl^- in aqueous phases.

In addition to lithium, magnesium, sodium and potassium, the salt lake brines contain considerable concentration of boron. The form of

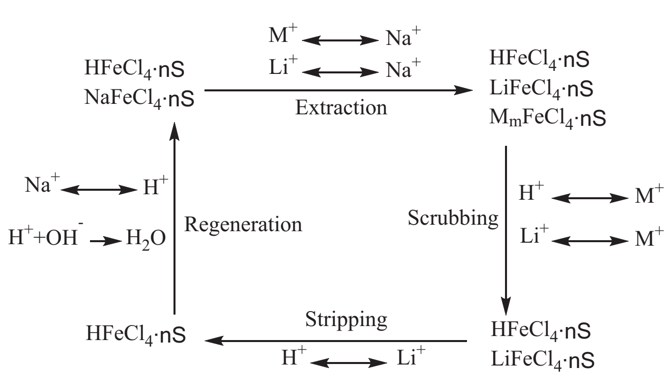

Fig. 1. Principle of the whole extraction cycle.

boron and borate in salt lake brine depends on the pH and boron concentration [25,26]. According to experience, boron should be first removed from brine before lithium recovery through acidification-crystallization or extraction process [27]. Xiang et al. studied the effect of boron on lithium extraction using TBP-$FeCl_3$-MIBK system, and the results showed that boron in brine promoted the extraction of lithium and magnesium, but reduced the separation factor between lithium and magnesium [28].

Centrifugal extractors offer various advantages which include high mass transfer coefficients, high interfacial areas, low residence times and clear separation of phases after extraction. Owing to these features, centrifugal extractors had been widely applied in radiation chemistry [29,30], biological operations [31,32], and metal ion separation [33–36]. Application of centrifugal extractors in extraction lithium from salt lake brine has not yet been reported.

Considering the cost, the low price of H_3BO_3 makes it a disadvantage to separate out H_3BO_3 completely before lithium recovery. In this paper, we focus on extraction process of lithium from salt lake brine containing boron based on our previous works. The effect of boron concentration in brine and the organic phase component on extraction efficiency of lithium, magnesium and boron was explored. Countercurrent extraction, scrubbing and stripping experiments were performed to optimize the lithium recovery process. The whole extraction process using traditional separating funnels was also conducted. Centrifugal extractors were used in the magnified experiment of the entire extraction process. Our study provides a convenient route for lithium recovery from salt lake brine containing high concentration of boron and magnesium.

2. Experimentation

2.1. Materials and instruments

$LiCl\cdot H_2O$ (purity > 97%; Sinopharm Chemical Reagent Co.), $MgCl_2\cdot 6H_2O$ (purity > 98%; Tianjin Kemi'ou Chemical Reagent Co.), $FeCl_3\cdot 6H_2O$ (purity > 99%; Sinopharm Chemical Reagent Co.), TBP (purity > 98.5%; Sinopharm Chemical Reagent Co.), Hydrochloric acid (A.R.; Sichuan Xilong Chemical Co.), NaOH (purity > 96%; Tianjin Kemi'ou Chemical Reagent Co.) and H_3BO_3 (purity > 99.5%; Tianjin Kemi'ou Chemical Reagent Co.) were used. Kerosene (260#; Beijing Sinopec Chemical Reagent Co.) and N523 (purity > 97%; supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.) were also used. Simulated brine was prepared by $MgCl_2\cdot 6H_2O$, $LiCl\cdot H_2O$ and H_3BO_3. The salt lake brine was obtained from Qinghai Citic Guoan Technology Development Co, and the components of the brine were shown in Table 1.

The instruments were used as follows: strong shaker (SR-2 DW; TAITEC), centrifuge (TDL-40B-W; Shanghai Anting Scientific Instrument Factory), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (ICAP6500 DUO; America Thermo Scientific), atomic absorption spectrometer (AAS) (A3F-12; Beijing Purkinje General Instrument Co.) and other glassware. Centrifugal extractors and Mixer settlers used to extraction lithium were customized by Beijing institute of extraction applied technology. The major technical parameters of centrifugal extractors were listed in Table 2. Mixer settlers were made of PVDF, the volume of mixing and clarifying chamber was 400 mL and 1600 mL respectively.

Table 1
Components of the adjusted salt lake brine.

Component	Li^+	H_3BO_3	Mg^{2+}	Na^+	K^+	Ca^{2+}	Cl^-	pH
Concentration (g/L)	2.32	15.46	113.85	5.41	0.93	0.068	356.32	4.65