



Extraction of lithium from salt lake brine containing borate anion and high concentration of magnesium



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ABSTRACT

Lithium recovery from salt lake brine with a high magnesium/lithium concentration ratio from Qinghai province, China, was investigated. Li^+ extraction was performed using tributyl phosphate in methyl isobutyl ketone as the extractant and FeCl_3 as the coextractant. An extraction mechanism, based on cation exchange of Li^+ and Mg^{2+} with H^+ and Na^+ , was proposed. Boron exists as $\text{B}(\text{OH})_4^-$ in salt lake brine and is extracted into organic phase as boric acid. $\text{B}(\text{OH})_4^-$ in salt lake brine can strip H^+ from the regenerated organic phase; this results in extraction of larger amounts of Li^+ and Mg^{2+} because of electroneutrality. Based on cation exchange mechanism and neutralization of $\text{B}(\text{OH})_4^-$ with H^+ , the extraction behaviors of Li^+ and Mg^{2+} from salt lake brine are successfully predicted. An experiment using a five-stage mixer-settler with countercurrent flow was conducted. The results showed that $\text{B}(\text{OH})_4^-$ largely favors lithium extraction from salt lake brine.

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1. Introduction

Lithium is the lightest solid element, and it has important applications in lithium-ion batteries (Tarascon 2010). With the development of electric vehicles, the demand for lithium is increasing (Grosjean et al. 2012; Gruber et al. 2011). Lithium is mainly acquired from two sources: minerals and salt lake brines (Will 1996). Due to lower cost and more available reserves, recovery of lithium from salt lake brines has been a trend in lithium recovery industry. Recovery of lithium from salt lake brine is complicated by the presence of other elements especially magnesium. Magnesium/lithium ratio (Mg/Li ratio) varies significantly among brine deposits worldwide, with the highest in USA, Israel and China (Vikström et al. 2013). Because of process complexity, significant lithium resources in salt lake brines with high Mg/Li ratios have not been recovered effectively (Kesler et al. 2012).

Recent research on the recovery of lithium from salt lake brines with high magnesium concentrations has focused on extraction (Sun et al. 2011; Yang et al. 2013; Zhou et al. 2013; Zhou et al. 2011a; Zhou et al. 2012; Zhou et al. 2011b), adsorption (Özgür 2010; Zhang et al. 2007), electrodialysis (Hoshino 2013), nanofiltration (Bi et al. 2014; Wen et al. 2006) and membrane extraction (Song et al. 2014). Among these methods, extraction, which has the advantages of easy operation and energy saving, is attracting increasing attention. Tributyl phosphate (TBP) is the most widely used extractant. Lithium is often extracted by coextraction with a kind of hydrophobic anion (e.g., FeCl_4^- , ClO_4^- , $\text{B}(\text{C}_6\text{H}_5)_4^-$) (Kuz'min and Gudkova 2015; Yang et al. 2013; Zhou et al.

2012). To prevent formation of third phase, polar diluent is preferred (Zhou et al. 2012). Zhou et al. found that tributyl phosphate (TBP)/ FeCl_3 in methyl isobutyl ketone (MIBK) is an effective extractant for lithium recovery from salt lake brines containing high concentration of MgCl_2 (Zhou et al. 2013; Zhou et al. 2011a; Zhou et al. 2012). An extraction process has been proposed based on the extraction behaviors of simulated experimental systems (Zhou et al. 2012). Li et al. carried out a pilot experiment in an eight-stage mixer-settler using TBP/ FeCl_3 in N,N-di(2-ethylhexyl)acetamide/kerosene, the extraction efficiency of lithium reached 96% (Shi et al. 2013).

In addition to lithium and magnesium, the treated salt lake brines may contain significant concentrations of potassium, sodium, and boron. Zhou et al. compared the competitive sequences for several cations using TBP/ FeCl_3 in MIBK as the extractant (Zhou et al. 2012). However, quantitative correlations for competing ion extractions, which are crucial in industrial design, were not reported.

Typically boron is first removed from salt lake brine before lithium recovery. And the effect of boron on lithium extraction has not been reported. Gao et al. found that boron exists as borate anions in salt lake brine, and the form of the borate anion depends on the pH and the boron concentration (Gao et al. 2000; Xia et al. 1989). Jia et al. studied the hydrochloric acid–pH titration curves of salt lake brines from Qinghai and found that they were similar to those for titration of a strong base with a strong acid (Jia et al. 2000). They also used Fourier-transform infrared spectroscopy to investigate the possible forms of borate anions in brines, and concluded that $\text{B}(\text{OH})_4^-$ and polyborate anions could exist. Boron in salt lake brines can be recovered by extraction; aliphatic 1,3-diols (Egneus and Uppström 1973), substituted salicyl alcohol (Ayers et al. 1981), and *tert*-butylcatechol (Grinstead 1972) are

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effective extractants. The mechanism involves reaction of boric acid or borate ions with the alcohol to form neutral or anionic complexes, which are highly soluble in the organic phase.

In this study, the extraction of lithium from salt lake brine was investigated. By comparing extraction properties of salt lake brine with that of simulated brine, the effects of borate anion and other metal cations, i.e., Ca^{2+} , K^+ , Na^+ , and Mg^{2+} , were determined, and the extraction mechanism was clarified. The extraction performance of lithium from salt lake brine in a five-stage mixer-settler with countercurrent flow was also studied. The findings may help provide a new routine for lithium recovery from salt lake brine containing borate anions and high concentration of magnesium.

2. Materials and methods

2.1. Materials

The following analytical reagents were used: LiCl (purity >97%) from Shanghai Jufeng Science Co., Ltd.; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (purity >98%) from Tianjin Kemiou Chemical Reagent Co., Ltd.; MIBK (purity >99%) from Tianjin Yongda Chemical Reagent Co., Ltd.; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (purity >99%) and TBP (purity >98.5%) from Sinopharm Chemical Reagent Co., Ltd.; HCl (concentration 36–38 wt%) and $\text{B}(\text{OH})_3$ (purity >99.5%) from Beijing Chemical Works; NaOH (purity >96%) and NaCl (purity >99.5%) from Beijing Modern Oriental Fine Chemistry Co., Ltd. The treated salt lake brine was obtained from Qinghai Salt Lake Industry Co., Ltd., China. The brine composition is presented in Table 1.

2.2. Methods

All extraction experiments were conducted in 50 mL separating funnels at 25 ± 2 °C. Organic phases consisting of 40% TBP/MIBK (by volume) and 0.1 mol/L FeCl_3 were used in all experiments. The volume ratio of the organic phase to the aqueous phase, $R(\text{O}/\text{A})$, was kept at 1. In each extraction equilibrium experiment, the separating funnel was shaken by hand for about 10 min and then left to settle for 30 min, during which the two phases separated. Preliminary experiments showed that equilibrium was reached within 10 min. Organic and aqueous phase samples were then taken from the separating funnels for solute concentration analysis.

The regenerated organic phase was prepared by three steps: extraction, stripping and regeneration. In extraction step, 40% TBP/MIBK was equilibrated with equal volume aqueous phase containing 0.05 mol/L LiCl + 3.5 mol/L MgCl_2 + 0.1 mol/L FeCl_3 , and the organic phase containing 0.1 mol/L LiFeCl_4 + $\text{Mg}_{0.5}\text{FeCl}_4$ was prepared. Then the organic phase was twice stripped with 3 mol/L HCl at $R(\text{O}/\text{A}) = 10$. After stripping, only HFeCl_4 existed in the organic phase. In regeneration step, 5 mol/L NaCl solution containing different molar concentration of NaOH (0–0.14 mol/L) was used to strip H^+ from the organic phase at $R(\text{O}/\text{A}) = 1$. And a series of organic phases with various molar ratios of NaFeCl_4 to HFeCl_4 , $R_{\text{Na}/\text{H},\text{org}}$, were obtained.

Table 1
Composition of treated Salt Lake Brine.

Substance	Concentration/(mol/L)
Li^+	0.050
Mg^{2+}	4.739
Na^+	0.082
K^+	0.020
Ca^{2+}	0.001
B	0.036
SO_4^{2-}	0.121
Cl^-	9.431

The effect of borate anions was investigated using simulated brine with or without borate anions, with the same concentrations of lithium and magnesium to the salt lake brine.

An MSU-0,5 laboratory mixer-settler unit (MEAB Metalextraktion AB) was used to extract lithium from the salt lake brine and simulated brine using TBP/ FeCl_3 in MIBK.

2.3. Analysis

The cation concentrations in the aqueous samples were determined using optical atomic absorption spectrometry (Z-5000-AAS, Hitachi, Tokyo, Japan). The anion concentrations in the aqueous samples were determined using ion chromatography (ICS-1100, Dionex). The cation concentration loaded in the organic phase was determined by washing the organic phase with an equal volume of distilled water to remove all cations, and then the concentrations of Li^+ , K^+ , Na^+ , and Ca^{2+} in the stripping aqueous phase were determined. The brine contains high concentration of magnesium, therefore even a low degree of entrainment considerably increases the magnesium concentration in the organic phase. To eliminate the entrainment effect, the concentration of magnesium in the organic phase is determined using the charge conversation equation:

$$[\text{Mg}(\text{FeCl}_4)_2 \cdot 2n\text{TBP}]_{\text{org}} = \frac{[\text{FeCl}_4^-]_{\text{total,org}} - [\text{LiFeCl}_4 \cdot n\text{TBP}]_{\text{org}} - [\text{NaFeCl}_4 \cdot n\text{TBP}]_{\text{org}} - [\text{HFeCl}_4 \cdot n\text{TBP}]_{\text{org}}}{2} \quad (1)$$

The boron concentration in the aqueous phase was determined using inductively coupled plasma optical emission spectrometry (IRIS Intrepid II XSP, Thermo Fisher, USA). The H^+ concentration was determined using an automatic potentiometric titrator (T50 series, Mettler-Toledo, Greisensee, Switzerland) based on pH titration curve. A combined glass pH electrode with a ceramic frit (EG11-BNC, Mettler-Toledo, Greisensee, Switzerland) was connected with the titrator to measure solution pH. The electrode was calibrated with pH = 7.00 and 4.01 standard buffer solutions by two point calibration method.

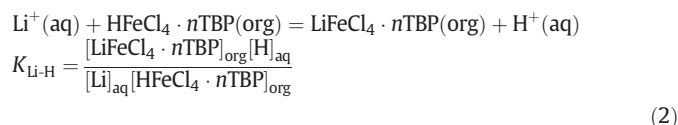
3. Results and discussion

3.1. Unique extraction properties of salt lake brine

Extraction of brine was carried out using the organic phase (40% TBP/MIBK, 0.1 mol/L FeCl_3) where Na^+ and H^+ were present. To compare the extraction properties of salt lake brine with simulated brine, a series of organic phases with various molar ratios of NaFeCl_4 to HFeCl_4 , $R_{\text{Na}/\text{H},\text{org}}$, were prepared. The extractabilities of Li^+ and Mg^{2+} from salt lake brine and simulated brine consisting of LiCl + MgCl_2 are shown in Fig. 1. The results (Fig. 1) show that the Li^+ and Mg^{2+} concentrations in the organic phase both increase with increasing $R_{\text{Na}/\text{H},\text{org}}$. This indicates that the exchange abilities of Li^+ and Mg^{2+} with Na^+ are clearly larger than that with H^+ . Though simulated brine contains almost the same concentrations of LiCl and MgCl_2 to salt lake brine, the extractabilities of Li^+ and Mg^{2+} are significantly larger for salt lake brine.

3.2. Extraction mechanism for simulated brine

The extraction mechanism for the simulated brine consisting of MgCl_2 + LiCl is the cation exchange of Li^+ and Mg^{2+} with Na^+ and H^+ ; the reactions can be written as:



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