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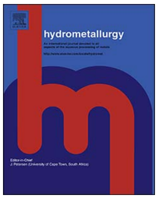

Technical note

Hydrometallurgical processing of lithium, potassium, and boron for the comprehensive utilization of Da Qaidam lake brine via natural evaporation and freezing

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ABSTRACT

A strategy for the hydrometallurgical processing of potassium, boron, and lithium for the comprehensive utilization of Da Qaidam lake brine based on freezing and natural evaporation was developed. This process involves five major crystallization steps: remove sulfate by crystallizing mirabilite at low temperature, deposit carnallite through natural evaporation, enrich boron and lithium by eliminating magnesium through the addition of mirabilite and further evaporation, crystallize borate by brine dilution, and crystallize lithium sulfate monohydrate through further evaporation. In this study, potassium, boron, and lithium salt deposits with relatively high grades and yields were obtained through the controlled crystallization processes. This process provides a feasible and environmentally-friendly alternative for the comprehensive utilization of the Da Qaidam lake brine.

1. Introduction

Salt lake brines are important potassium, boron and lithium resources. Extracting the valuable elements is the major goal of the brine industry. For this purpose, many processes, e.g., fractional crystallization (da Silva et al., 2017; Gao et al., 2015; Liu et al., 2017; Quist-Jensen et al., 2016), solvent extraction (Kumar et al., 2015; Zhang et al., 2016), adsorption (Xiao et al., 2011), precipitation (Perez and Barrientos Ruiz, 2013), membrane filtration (Somrani et al., 2013; Nie et al., 2017; Ma and Guo, 2016), and calcination-leaching (Yang et al., 1996), have been introduced. Among these processes, crystallization is a conventional but effective approach for salt separation and trace element enrichment in massive brine processing.

Da Qaidam Lake, which is located in the Qinghai-Tibet, northwestern China, is a typical sulfate-type salt lake in which potassium, boron, and lithium are enriched. For extracting these valuable elements from the Da Qaidam lake brine, a large amount of fundamental research work has been conducted in the past decades. The crystallization sequences of Da Qaidam brine in summer and winter have been determined (Gao and Liu, 1996a; Gao and Liu, 1996b). The degree of boron concentration in the $MgCl_2$-saturated bittern and the dilution behavior of brine containing high concentration boron (Gao and Feng, 1992; Peng, 2016) have also been studied. However, the crystallization of lithium sulfate and a complete technical scheme have never been reported. In the previous technique for Da Qaidam lake brine, salts were crystallized through direct evaporation from summer brine, which resulted in a mixture of $KCl{\cdot}MgCl_2{\cdot}6H_2O$ and $MgSO_4{\cdot}7H_2O$ precipitated. Additionally, the lithium can only be concentrated to approximately 0.2% in the $MgCl_2$-saturated bittern during direct evaporation and the extraction of lithium from the bittern has never been implemented using crystallization process.

Balancing the industrial economic value and the fragile ecological environment on the Tibetan Plateau is extremely important. Thus, using natural solar evaporation pond techniques adapted to the climate and other local factors may be a good strategy for harvesting salt deposits of potassium, boron, and lithium with relatively high grades (Meng et al., 2014; Zhu et al., 2014). This study proposed a novel technique involving systematic fractional crystallization processes for the comprehensive utilization of Da Qaidam lake brine and obtained high-grade potassium, borate, and lithium salts just using solar evaporation pond techniques, including natural brine freezing, natural evaporation, and dilution and mixing of brine.

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Table 1
Densities, masses, Mg/Li ratios, and chemical compositions of the brines used in the experiments.

Brine index	Density/ g·mL^{-1}	Chemical composition (wt%)							Mg/Li
		Na^+	K^+	Mg^{2+}	Cl^-	SO_4^{2-}	Li^+	B_2O_3	
A	1.2367	5.22	0.76	3.04	15.22	3.24	0.0233	0.227	130
B	1.2054	4.05	0.75	3.02	15.12	0.91	0.0231	0.226	130
C	1.3451	0.08	0.06	8.98	24.38	2.73	0.0938	0.846	96
D	1.3388	0.77	0.36	6.47	15.41	7.27	0.609	5.314	11
E	1.1440	0.64	0.19	3.01	8.19	3.92	0.304	0.515	10
F	1.3052	0.60	0.37	6.82	20.60	3.56	0.546	1.407	12
E2	1.1434	0.12	0.07	3.37	9.71	2.58	0.338	0.378	10
F2	1.2834	2.66	0.25	4.05	13.44	9.85	1.008	1.148	4
G2	–	–	0.07	8.88	22.95	3.52	0.280	3.521	32

2. Materials and methods

The raw brine (Brine A) was collected from Da Qaidam lake in summer. The density and composition of the raw brine are listed in Table 1. The process for crystallizing lithium, potassium, and boron from Da Qaidam lake brine using natural evaporation and freezing was conducted as shown in Fig. 1.

The lithium content was determined by flame atomic absorption spectrometry. K^+ was determined by a sodium tetraphenylboron-quaternary ammonium salt volumetric method, whereas, Ca^{2+} and Mg^{2+} were determined by disodium ethylenediamine tetraacetate (EDTA) volumetric titration. SO_4^{2-} was measured by a $BaSO_4$ gravimetric method, and Cl^- was determined by mercuric nitrate volumetric titration. The total boron content was evaluated by titration with NaOH solution, in the presence of mannitol using phenolphthalein as the indicator. The sodium content was calculated by the subtraction method based on the charge balance. All chemicals used in the study were analytical grade.

The web version of the ISLEC software, which includes a multi-temperature database of the seven component system Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} – H_2O was used to model the brine crystallization processes under different conditions (Li et al., 2016; Li, 2015).

3. Results and discussion

The masses and chemical compositions of brines used in the experiments are listed in Table 1.

3.1. Crystallization of mirabilite and removal of SO_4^{2-}

Solubility curves of $Na_2SO_4·10H_2O$ and $NaCl·2H_2O$ vs. the temperature were calculated by ISLEC software and are shown in Fig. 2. The solubility curves show that the solubility of $Na_2SO_4·10H_2O$ drops drastically as the temperature decreases; in contrast, the solubility of NaCl decreases slightly, and when the temperature is below 273.15 K, the solubility of $NaCl·2H_2O$ drops a little. When freezing brine saturated with NaCl and $Na_2SO_4·10H_2O$, NaCl and $Na_2SO_4·10H_2O$ will deposit first, and then, $NaCl·2H_2O$ will precipitate together with $Na_2SO_4·10H_2O$ as the temperature decreases. When the temperature is low enough, the brine will freeze as a block comprising a mixture of ice, $NaCl·2H_2O$, and $Na_2SO_4·10H_2O$. When diluted somewhat, the brine will be saturated only with $Na_2SO_4·10H_2O$. Pure $Na_2SO_4·10H_2O$ can be obtained by freezing in some temperature ranges.

Because Da Qaidam brine is of the magnesium sulfate type, its constituents cannot be simplified as Na^+ // Cl^-, SO_4^{2-} – H_2O. Thus, diagrams of the Na^+, Mg^{2+} // Cl^-, SO_4^{2-} – H_2O system at 295.15 K and 268.15 K (Niu and Cheng, 2001) have been introduced to reflect the solubility changes of $Na_2SO_4·10H_2O$ and $NaCl·2H_2O$ as the temperature decreases. Fig. 3 shows that the solubility of $Na_2SO_4·10H_2O$ drops drastically as the temperature decreases.

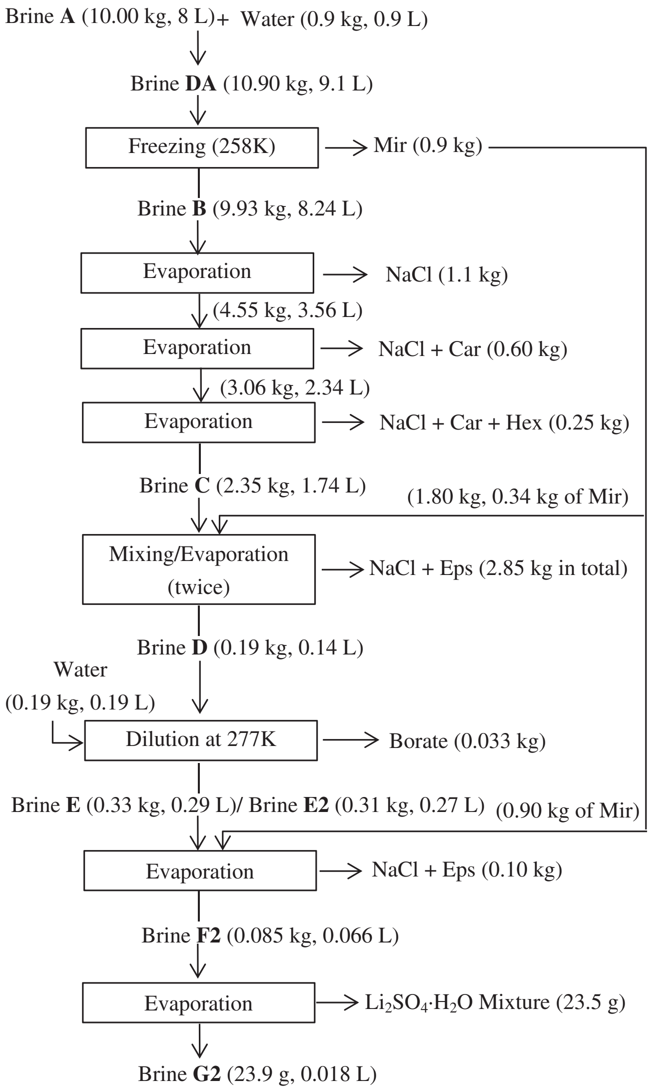

Fig. 1. Flowchart for the crystallization of potassium, boron, and lithium from Da Qaidam lake brine (Mir, $Na_2SO_4·10H_2O$; Car, $KCl·MgCl_2·6H_2O$; Hex, $MgSO_4·6H_2O$; Eps, $MgSO_4·7H_2O$).

It's complicated to calculate crystallization process according to the solubility isotherm of Na^+, Mg^{2+} // Cl^-, SO_4^{2-} – H_2O at different temperatures. Hence, we simulate the freezing process using ISLEC-web. The compositions of the frozen salts at 258.15 K from brine diluted with different masses of water and the removal rates of SO_4^{2-} from Brine A and DA after freezing at various temperatures were simulated by ISLEC-web and plotted in Fig. 4.

The simulated results showed that the removal rate of SO_4^{2-} from the brines increased drastically when the temperature dropped below 273 K. The salts precipitated was a mixture of $Na_2SO_4·10H_2O$ and $NaCl·2H_2O$ when Brine A was frozen, and the mixture became almost pure $Na_2SO_4·10H_2O$ when Brine A was diluted by 9% water. Additionally, the removal rates of SO_4^{2-} from the brines increased slightly when the brines were diluted. Indeed, according to the ISLEC simulation, approximately 90% of sulfate in Brine DA can be removed by crystallizing $Na_2SO_4·10H_2O$ at 258.15 K.

In the freezing experiment, a sample of **Brine DA** (10.0 kg of Brine A and 0.9 kg of water) in a plastic container was settled in a refrigerator at 257.65 K. The brine was disturbed by stirring once per day. Ten days later, many colorless flakes had crystallized in the bottom of the container, and the samples were separated by filtration. 0.90 kg of frozen