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Clean Separation Process of Chabocuo Saline Lake in Tibet

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1 Introduction

Chabocuo Lake is located in the territory of Gaize County Ali area Tibet, the altitude of the lake-surface is 4505 m with a total area of 32 Km^2. It is a typical sulfate type saline and rich in boron and lithium. In the natural evaporation process, several mineral sylvites cocrystallize out, thus increases the difficulties for separating and extracting potassium from the lake. In the final stage of the evaporation process, boron and lithium precipitate sporadically, and they can not be enriched in one phase. In liquid phase, Mg/Li ratio is too high to extract lithium. Without local industrial base and long distance transportation, the transportation cost of raw chemical materials to the locality to product boron and lithium is too high, so the enterprise can't make any profit. Based on the existing experience and technology, the development of the saline lake will face the following problems : (1) when potassium precipitates, associated minerals and sulfate minerals (sylvite, carnallite, kainite, soft leonite etc.) precipitate too much so it leads to the decrease in the quality and increase in the processing difficulty; (2) the problem of boron is that it's very difficult to enrich and extract .Using acid method to produce boric acid and alkali method to produce borax are expensive and not qualify for environmental protection; (3) the lithium problem is mainly due to the old brine's Mg/Li ratio is a little high so that boron concentration does not go up, and low grade lithium mineral was precipitated. In view of the above problems, a clean process of comprehensive utilization of brine resources in Chabocuo was designed. This process does not introduce foreign chemicals so it is cheap and environment friendly. This process is divided into the following steps: simplify brine system to obtain high grade potassium ore; add mirabilite to remove most magnesium to reduce the Mg/Li ratio; dilute to obtain the high grade magnesium borate solid mineral (once again reduced the ratio of magnesium to lithium); the last step is to control the conditions of high concentration of lithium solution with low Mg/Li ratio to precipitate high grade lithium sulfate.

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2 Experiments

2.1 Experimental materials

The brine (A-L0) used in the frozen nitrate experiment was collected from the Cabocuo lake, and live pre-concentrated to sodium chloride saturated stage. The bittern (B-L0) used in the later experiment was collected from the pilot pool of Cabocuo. The chemical composition are shown in Table 1.

Table 1 Compositions of the brines used in experiments (wt.%)

NO.	Na^+	Mg^{2+}	Li^+	K^+	Cl^-	SO_4^{2-}	B_2O_3
A^-L_0	7.28	0.465	0.019	1.31	12.55	1.68	0.100
B^-L_0	0.475	7.01	0.549	0.737	19.52	5.04	2.78

2.2 Experimental techniques

The freezing mirability and natural evaporation experiments were completed in the laboratory. The specific method is: Take 12.00 kg A-L0 brine to a plastic cube box, and control the temperature of the low temperature test chamber at -20.0 ℃ to freeze the brine for five days, then separate the solid-liquid phase under cold condition, continue to evaporate the brine at a temperature range of 19 -29 ℃. when the evaporation arrive a certain degree then conduct solid-liquid separation, The separated liquid phase need to be done chemical analysis and the separated solid phase need to be done chemical analysis and XRD characterization.

The precipitation experiment of boron and lithium was

completed beside Cabocuo Lake. The specific operation is: take 300 kg of B-L0 brine, add 220 kg of fresh water, then add 200 kg more fresh water halfway. After 35 days, separate the solid-liquid phase, and get the $2MgO{\cdot}3B_2O_3{\cdot}15H_2O$. Add mirabilite to the brine in order to reduce the Mg/Li ratio to a certain value. When lithium is close to saturation, naturally evaporate the brine to precipitate lithium. The whole process is shown in Figure 1.

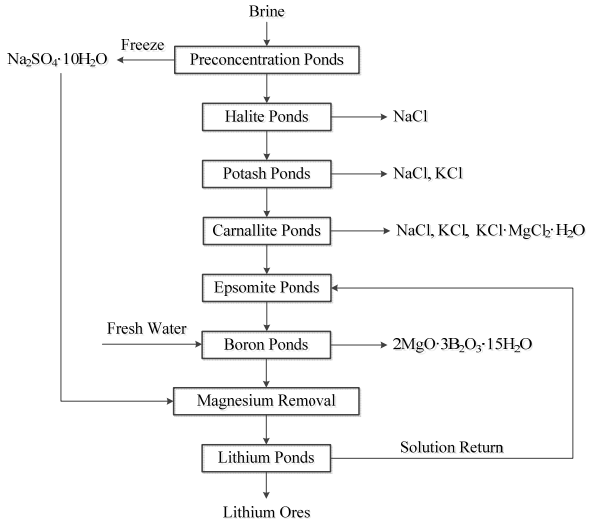

Fig. 1. Process flow diagram.

Table 2 Liquid compositions at freezing mirabilite and natural evaporation(wt.%)

No	Density g·mL⁻1	K^+	Mg^{2+}	B_2O_3	Cl^-	SO_4^{2-}	Li^+
A-L0	1.179	1.31	0.465	0.100	12.55	1.68	0.019
A-DL	1.167	1.32	0.489	0.105	13.30	0.168	0.021
A-L1	1.225	3.19	1.12	0.252	16.86	0.393	0.049
A-L2	1.240	4.66	1.75	0.394	17.52	0.621	0.076
A-L3	1.248	4.03	2.84	0.645	17.70	1.02	0.124
A-L4	1.302	1.99	6.50	1.52	20.47	2.12	0.297

2.3 Experimental analyses

The analytical methods were based on those given by the Analysis Method of Brine and Salt (1988). Lithium contents of the brines were analyzed by atomic absorption spectroscopy (AAnalyst 800, PE of USA) while others were analyzed by chemical analysis method. K^+ was analyzed using the gravimetric method; Mg^{2+} were analyzed by disodium ethylenediamine tetraacetate (EDTA) volumetric titration method; SO_4^{2-} was analyzed by the gravimetric method, using barium chloride; Cl^- was analyzed by the silver nitrate volumetric titration method; the concentration of borate ion was evaluated by titration with 0.03 mol/L NaOH, in the presence of mannitol, with phenolphthalein as the indicator. The content of sodium is calculated by the subtraction method in charge balance.

Table 3 Solid compositions at freezing mirabilite and natural evaporation(wt.%)

Stage	No	K^+	Mg^{2+}	B_2O_3	Cl^-	SO_4^{2-}	Li^+
Freeze	A-DS	0.52	0.120	0.027	3.36	20.99	0.005
NaCl	A-S1	0.66	0.293	0.052	53.13	0.043	0.009
	A-S2	1.99	0.183	0.042	56.33	0.056	0.008
KCl	A-S3	16.83	0.323	0.073	52.17	0.114	0.016
$MgCl_2{\cdot}KCl{\cdot}6H_2O$	A-S4	16.37	1.33	0.266	48.09	1.03	0.040

3 Results and discussion

3.1 Freezing mirabilite - natural evaporation experiments

12.00 kg NaCl saturated brine was frozen at -20.0 ℃, and 843 g solid was got. The frozen salt rate was 7.19%, containing 20.99% SO_4^{2-} in the solids, amount to contain 70.36% mirabilite, and the removal rate of SO_4^{2-} was 89.85%. After separation, naturally evaporate the liquid at normal temperature, and specific experimental data as follows.

According to the data of A-L4: Lithium concentration was 0.297%, boron concentration was 1.52%, enrichment factor of lithium and boron were basically the same, indicating that at this stage lithium and boron did not precipitate. The solid-phase data shows that in the potassium stage, only KCl and $MgCl_2{\cdot}KCl{\cdot}6H_2O$ were precipitated. While in the KCl stage, potassium content was 16.83% (KCl content of 32.09%), and at the $MgCl_2{\cdot}KCl{\cdot}6H_2O$ stage, potassium content was 16.37% (KCl content of 31.21%). The precipitated solid phase was identificated by XRD and the results were shown in Table 4.

Table 4 XRD identification results of solids

No	Identification results
A-DS	NaCl, Na_2SO_4（Drying）
A-S1	NaCl
A-S2	NaCl, KCl（Bit）
A-S3	NaCl, KCl
A-S4	NaCl、KCl、$KCl{\cdot}MgCl_2{\cdot}6H_2O$

The crystallization sequence of freezing mirabilite brine can be summarized from table 4 as following: The first stage is for NaCl; the second stage is for KCl; the third stage is for $KCl{\cdot}MgCl_2{\cdot}6H_2O$. In those stages, lithium and boron were not separated out from the brine. The crystallization sequence of salts of this brine is similar to that of Da Qaidam brine in winter (Gao et al., 1996).

3.2 Extracting boron experiments

Gao Shiyang academician found that there were different magnesium borate hydrate salts crystallized in the process of diluting high magnesium brine containing boron, which was known as “Salt Formation by Dilution” phenomenon

(Gao et al.,1986, 1992). In this experiment, extraction of boron from brine used fresh water. After potassium was precipitated out, the bittern was joined in fresh water, and solution composition changes were shown in table 5.

Table 5 Compositions changes of extracting boron process (wt.%)

	Na^+	Mg^{2+}	Li^+	K^+	Cl^-	SO_4^{2-}	B_2O_3
B-L0	0.475	7.01	0.549	0.737	19.52	5.04	2.78
B-L1	0.102	5.44	0.476	0.491	15.94	3.39	0.908

Table 6 Compositions of boron ores (wt.%)

	Na^+	Mg^{2+}	Li^+	K^+	Cl^-	SO_4^{2}	B_2O_3
B-S1	0.00	8.33	0.00	0.00	2.55	0.42	32.8

Data from Table 5 shows that Lithium concentration of B -L_1 was slightly lower than B-L_0, indicating that a small amount of water remained. In the process of boron removal, due to precipitation of the magnesium borate, Mg/Li ratio declined slightly. Data from table 6 shows that wet basis boron grade was up to 32.89%, after drying up it could get to 40%, and the boron yield was 62.83%. XRD results shows that the rock of boron was $2MgO·3B_2O_3·15H_2O$.

3.3 removal of magnesium

This experiment used B-L_1 brine, 90 kg B-L_1 brine and 38 kg mirabilite was added at one time (B-L_2). The water temperature was about 17 ℃. In winter the water temperature droped rapidly, continued to evaporate to precipitate magnesium, and the lowest night temperature was - 7 ℃ (B-L_4), later (B-L_8) the temperature dropped to -13 ℃. The composition changes of liquid and solids of this experiment were shown in table 7 and table 8 respectively. The data from table 7 shows that in the process of removing magnesium, boron didn'*t* precipitate when evaporating brine at low temperature,. At the late stage magnesium removal, the temperature was as low as -7 ℃, but it did not affect the removal of magnesium. Mg/Li ratio dropped to about 5:1. Lithium and boron further enriched, with lithium enriched to 1.01% and boron enriched to$_1$.91%, and the enrichment factors of these two elements were basically the

Table 7 Liquid compositions changes of removing magnesium process (wt.%)

No	Mg^{2+}	Li^+	K^+	Cl^-	SO_4^{2-}	B_2O_3	Mg/Li
B-L2	4.23	0.545	0.427	12.92	10.90	0.903	10.35
B-L3	4.37	0.577	0.590	13.91	7.97	0.955	7.58
B-L4	4.33	0.612	0.639	14.74	5.97	1.15	7.07
B-L5	4.73	0.763	1.01	15.46	4.80	1.44	6.21
B-L6	5.26	0.861	1.06	17.63	4.08	1.68	6.12
B-L7	6.06	1.02	0.862	19.13	3.26	1.96	5.92
B-L8	5.82	1.10	0.721	19.44	3.33	2.11	5.28

Table 8 Partial solid compositions changes of removing magnesium process (wt.%)

No	Na^+	Mg^{2}	Li^+	K^+	Cl^-	SO_4^{2}	B_2O_3
B-S3	15.8	5.75	0.09	0.10	13.1	38.6	0.25
B -S4	9.27	6.77	0.07	0.00	15.7	25.1	0.23
B -S5	9.13	7.45	0.03	0.00	15.5	27.6	0.08
B –S8	9.65	6.95	0.12	2.88	25.5	17.2	0.33

same. Combined with the solid phase chemical analysis, it proved that in this process lithium and boron did not precipitate. XRD results show that in the earlier stage (B^-S_3), $Na_2SO_4·MgSO_4·15H_2O$ appeared, then $MgSO_4·6H_2O$ (B^-S_5) was crystallized, and in the last stage, $MgCl_2·6H_2O$ (B^-S_8) was crystallized. Magnesium removal rate was more than 80% in this experiment.

3.4 Precipitate lithium

After removing magnesium, continued to evaporate the solution naturally to precipitate lithium. The data are shown in table 9.

The data of table 9 shows that, after removing most of the boron and magnesium, the concentration of lithium can be enriched to 1.1%, lithium content was 3.31% in the Wet basis of solid phase, and 3.58% in the dry base, and the yield was 47.74%. Because boron precipitation was not completed previously, boron was enriched during the process of removing magnesium to 2.9%, together with the low temperature, boron was separated out. This affected the purity and grade of lithium, and probably will further affect the purification of lithium. The XRD indentification result of rough lithium ores are NaCl, $MgCl_2·6H_2O$, $Li_2SO_4·H_2O$ and $KCl·MgCl_2·6H_2O$, without other forms of lithium.

Table 9 Compositions changes of precipitating lithium process (wt.%)

No	Mg^{2+}	Li^+	K^+	Cl^-	SO_4^{2-}	B_2O_3	Mg/Li
B-L9	5.48	1.08	0.314	20.33	2.91	2.33	5.06
B-L10	6.67	1.03	0.216	21.48	2.22	2.51	6.45
B	7.11	0.982	0.0774	23.13	1.29	2.75	7.24
B-L12	7.55	0.915	0.0348	24.22	0.809	2.85	8.25
B-L13	7.57	0.909	0.0457	24.26	0.368	2.89	8.32
B-S13	6.04	3.31	4.82	25.00	18.97	1.60	

4 Conclusions

(1) The crystallization sequence of freezing mirabilite brine was : NaCl → NaCl + KCl → NaCl + KCl + $KCl·MgCl_2·H_2O$. In the process of evaporation, potassium didn'*t* precipitate in the form of sulphate, and boron and lithium enriched in the brine with the same enrichment factor.

(2) Added water to brine to precipitate boron, the concentration of boron decreased to 0.908% and the boron precipitation rate was 62.83%。

(3) Added mirabilite to the bittern, Mg/Li ratio significantly reduced to 5.28.

(4) In the process of natural evaporation, the grade of lithium ore precipitation was 3.58%（33.00% $Li_2SO_4 \cdot H_2O$）, and the precipitation rate of lithium was 47.74%.

(5) The whole process without any addition of chemicals completed a preliminary separation of potassium, boron, and lithium. a single form of potash ore, high purity inderite ore, and lithium sulfate minerals were obtained.

Key words: Chabocuo, Sulfate-type, freezing mirabilite, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$, clean separation

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