Experimental study of isothermal evaporation of Lhaguo Tso Salt Lake in Tibet at 0°C

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ABSTRACT

The research shows that the original compositions of the brine of Lhaguo Tso Salt Lake in Tibet is located in the mirabilite region of isothermal phase diagram of the Li^+, Na^+, $K^+//Cl^-$, SO_4^{2-}-H_2O quinary system at 0°C, and the isothermal evaporation process is divided into four stages. The first section is the unsaturated section except for carbonate, the second section is the sodium salt section, the third section is the potassium salt section, the last section is the lithium salt section. Among them, the sodium chloride and the potassium chloride will be precipitated with the evaporation process after precipitation, the borax is precipitated gradually, and the lithium salt is precipitated in various forms. This study can provide a basic theoretical basis for the development and utilization of salt lake resources under low temperature conditions.

Keywords: Salt lake brine; Low-temperature; UNIQUAC model; Li-rich system

1. Introduction

At present, the relevant state departments have put forwards the call to speed up the development of domestic lithium resources. Many enterprises are quickly joining the army of lithium resource development and utilization, especially in the field of lithium extraction from salt lakes [1–7].

Lhaguo Tso Salt Lake is located in Mami Township, Gaize County, Ali Prefecture, Tibet, approximately 60 km away from Gaize County. It is an inland closed salt lake, roughly elliptical in shape, 12–18 km long from east to west, and 5–8 km wide from north to south. The surface of brine is approximately 4,470 m above sea level [8]. The average density of brine is 1.040 g/cm³, and the average pH is 9.351. Lhaguo Tso Salt Lake belongs to the sulfate type saline. The transportation around Lhaguo Tso Salt Lake is convenient, with national highways passing through, and a power grid

has been erected nearby, which is very beneficial to the development and utilization of Lhaguo Tso Salt Lake [9].

According to the "Detailed Investigation Report on Lithium (Boron, Potassium) Mine in Salt Lake Surface Brine in Lhaguo Mining Area, Gaize County, Tibet Autonomous Region" (2012) by the Fifth Geological Brigade of the Tibet Autonomous Region Geology and Mineral Exploration and Development Bureau, LiCl resources are 2.4 million tons, B_2O_3 resources are 3.8 million tons, KCl resources are 7.4 million tons. Lhaguo Tso Salt Lake has an extremely low magnesium–lithium ratio. It is rich in rare elements with huge potential value, which lays a solid foundation for the development and utilization of Lhaguo Tso Salt Lake.

Lhaguo Tso Salt Lake has not yet been industrially developed, but its resource endowment is very good at home and abroad, and it is currently a rare high-quality salt lake to be developed in China [10]. The average annual temperature in the county in the Ali Region of Tibet was between

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0.9°C~1.8°C, close to 0°C [11,12]. The characteristics of the magnesium–lithium ratio and low impurity content make it unique for lithium extraction from salt lakes. However, at the same time, we should also see that due to the limitations of industrialization in Tibet in terms of process design, energy security, national unity, environmental protection audit, employee recruitment, and backwards infrastructure, the industrial development of the brine resources of Lhaguo Tso Salt Lake is still a daunting task [13]. Therefore, it is extremely important and necessary to conduct basic research on the process design of salt lake brine resource development and utilization as soon as possible, and the isothermal evaporation experiment of salt lake brine is one of the core contents of all basic research [14,15].

2. Experimental procedures

2.1. Experimental reagents

NH_4Cl reagent was purchased from Shanghai Macklin Biochemical Co., Ltd., (China). $C_{10}H_{14}N_2Na_2O_8$ (EDTA), $C_6H_{14}O_6$, NaOH, $C_{24}H_{20}BNa$ and KCl were purchased from Sinopharm Chemical Reagent Co., Ltd., (China). The experimental water is a secondary water treated by an ultra-pure water processor ($\rho \geq 18$ MΩ/cm, pH = 7.33 ± 0.2). All chemicals were used as received. All reagents used are analytically pure.

2.2. Experimental process

A total of 100 kg brine of Lhaguo Tso Salt Lake was studied at 0°C isothermal evaporation experiment in a climate simulated constant greenhouse (±2°C), and an RCW-360 thermometer (±0.1°C) was used to detect the change in temperature of the brine. The compositions of the samples were measured by X-ray powder diffraction (XRD) identification analysis and inductively coupled plasma-atomic emission spectroscopy (ICP-OES), the temperature and density of the separation phase were recorded at each separation stage [16].

The chemical compositions of the brine (the original brine) are shown in Table 1.

2.3. Characterization

The crystal structures of the samples were measured by XRD on an XRD 6100 (Shimadzu, Japan) with Cu-Kα radiation. The concentration of metal ions (K^+, Na^+ and Li^+) was determined by ICP-OES [17]. The concentrations of anions, including Cl^- and SO_4^{2-}, were tested by mercury quantity, $BaCl_2$ weight and pH disposal methods, respectively. The EDTA complexity method was used to measure the concentrations of Ca^{2+} and Mg^{2+}. The concentrations of Rb^+ and Cs^+ were analysed by atomic absorption spectrum analysis. The specific analysis method operation is based on the analysis method of brine and salt [18].

3. Results and discussion

3.1. Physical–chemical parameters of Lhaguo Tso Salt Lake during the separation stages at 0°C

Evaporation experiments, including density, pH, water loss rate, brine production rate, and salt precipitation rate, were completed to investigate the impact of evaporation on the physical chemical parameters, as shown in Table 2.

The solid and liquid samples obtained by liquid–solid separation during isothermal evaporation at 0°C of Lhaguo Tso Salt Lake were subjected to chemical analysis. The liquid phase composition is shown in Table 3, and the solid phase composition is shown in Table 4.

The XRD patterns of samples obtained from the solid and liquid separation stages during the isothermal evaporation process are shown in Fig. 1 and Table 5.

From Tables 3, 4 and Fig. 1 it can be seen that the 0°C isothermal evaporation process of the Lhaguo Tso Salt Lake

Table 1
Chemical compositions of brine (Lhaguo Tso Salt Lake)

Element (Z-L0)	%
K^+	0.23
Na^+	1.51
Mg^{2+}	0.07
Ca^{2+}	0.006
Li^+	0.0306
B_2O_3	0.25
Cl^-	1.18
SO_4^{2-}	1.95
Rb^+	0.00066
Cs^+	0.00093

Table 2
Separation parameters of solid–liquid at 0°C isothermal evaporation of Lhaguo Tso Salt Lake

Numbering	Evaporation stage	Density (g/cm³)	pH	Water loss rate (%)	Brine production rate (%)	Salt precipitation rate (%)
Z-L0	Unsaturated section (except carbonate)	1.0430	9.321	0	100	0
Z-L1	Saturated mirabilite	1.0842	9.216	49.08	39.21	11.71
Z-L2	Sodium chloride saturated	1.1055	9.173	85.28	12.37	2.35
Z-L3		1.1612	9.247	90.8	7.85	1.35
Z-L4	Potassium chloride saturation	1.1638	9.166	92.77	5.73	1.50
Z-L5	Glaserite saturation	1.1888	8.997	95.65	3.98	0.37
Z-L6	Lithium salt saturation	1.2408	8.755	97.14	2.76	0.10

Table 3
Chemical composition of the liquid phase at 0°C isothermal evaporation experiment of Lhaguo Tso Salt Lake (%)

Samples	Chemical composition of liquid phase (%)									
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Li^+	B_2O_3	Cl^-	SO_4^{2-}	Rb^+	Cs^+
Z-L0	0.23	1.51	0.07	0.006	0.0306	0.25	1.18	1.95	0.00066	0.00093
Z-L1	0.64	4.36	0.20	0.011	0.075	0.87	3.25	5.82	0.00187	0.00191
Z-L2	1.71	7.00	0.23	0.016	0.19	0.93	9.00	5.31	0.00450	0.00519
Z-L3	2.11	5.85	0.28	0.016	0.23	0.67	9.01	1.30	0.00553	0.00629
Z-L4	2.18	6.06	0.21	0.012	0.24	0.64	15.02	1.35	0.00574	0.00656
Z-L5	2.39	6.73	0.25	0.011	0.27	0.71	18.95	1.52	0.00639	0.007
Z-L6	3.54	7.64	0.30	0.011	0.41	0.61	15.47	2.23	0.0154	0.0154

The analysis uncertainty for ion concentrations is 0.005.

Table 4
Solid phase chemical composition of Lhaguo Tso Salt Lake at 0°C isothermal evaporation experiment

Samples	Solid phase chemical components (%)									
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Li^+	B_2O_3	Cl^-	SO_4^{2-}	Rb^+	Cs^+
Z-S3	0.42	13.04	0.15	0.024	0.03	0.25	1.97	5.63	0.00051	0.0013
Z-S4	0.82	4.93	0.93	0.028	0.034	0.26	2.51	12.65	0.00481	0.0055
Z-S5	0.93	2.91	0.91	0.04	0.05	0.63	8.12	15.26	0.002	0.0025
Z-S6	1.72	29.48	0.76	0.045	0.075	0.78	13.26	11.37	0.0006	0.00094
Z-S7	3.16	16.13	0.07	0.027	0.16	0.93	38.23	17.43	0.00234	0.0024
Z-S8	10.69	24.43	0.67	0.063	0.23	0.67	45.89	3.55	0.00318	0.0029

The analysis uncertainty for ion concentrations is 0.005.
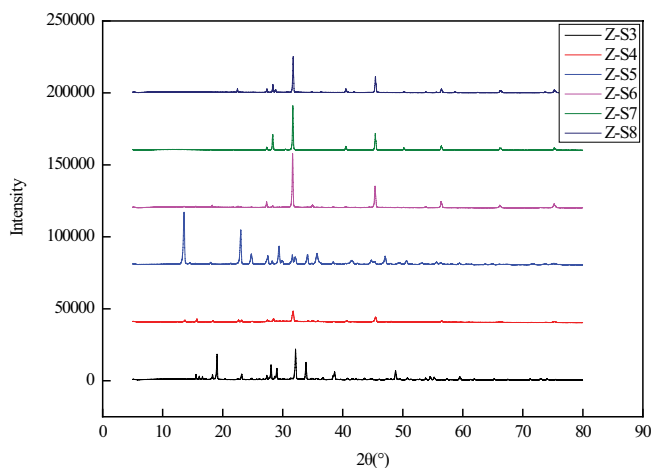

Fig. 1. X-ray powder diffraction patterns of solid phase samples at 0°C isothermal evaporation of Lhaguo Tso Salt Lake.

Table 5
Samples were measured by X-ray powder diffraction patterns during 0°C isothermal evaporation of Lhaguo Tso Salt Lake

Sample serial number	X-ray powder diffraction identification results
Z-S1	$Na_2SO_4 \cdot 10H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $MgCO_3 \cdot 3H_2O$
Z-S2	$NaCl$, $MgCO_3 \cdot 3H_2O$, $Na_2B_4O_7 \cdot 10H_2O$
Z-S3	$NaCl$, $MgCO_3 \cdot 3H_2O$
Z-S4	$NaCl$, KCl, $MgCO_3 \cdot 3H_2O$, $Na_2B_4O_7 \cdot 10H_2O$
Z-S5	$NaCl$, KCl, $Na_2SO_4 \cdot 3K_2SO_4$
Z-S6	$NaCl$, KCl, $Li_2SO_4 \cdot K_2SO_4$

can be roughly divided into four stages. However, there is a significant difference between the evaporation rules under room temperature conditions, which is mainly reflected in the precipitated nodes of each salt mineral, precipitated types and water loss rate. The first evaporation phase is the unsaturated section except carbonate; the second evaporation phase is the sodium salt section, mainly mirabilite and stone salt, and borax at the same time. The water loss rate is 23.08%, and the brine production rate is 76.92%. The third evaporation stage is the potassium salt segment, mainly potassium salt and glaserite, with a water loss rate of 74.83%, a brine production rate of 6.79%, and a salt precipitation rate of 18.38%. The last evaporation phase is a lithium salt section, mainly for lithium potassium sulfate and potassium sodium lithium sulfate ($Li_2SO_4 \cdot K_2SO_4 \cdot Na_2SO_4$). At this time, the water loss rate is 75.98%, the brine production rate is 4.49%, and the salt precipitation rate is 19.53%. Among them, NaCl and KCl precipitated with the evaporation process after precipitation.

3.2. Change in various ions in each stage during the 0°C isothermal evaporation

During the evaporation temperature at 0°C, the trend of changes in the concentration of major ions and trace ions concentrations during the separation phase of each solid and liquid is shown in Figs. 2 and 3.

In Figs. 2–5 it can be seen that the concentration of each ion is continuously concentrated in the unsaturated section (except carbonate) during the isothermal evaporation process at 0°C. When the water loss rate was approximately 23.08%, the mirabilite was saturated and precipitated in large quantity, and the contents of sulfate and sodium ions decreased significantly. At the same time, the lithium salt is brought out by the mother liquor with the precipitation of the sulfate, which causes the lithium ion concentration in

the liquid phase to be significantly reduced, indicating that the precipitation of the sulfate is extremely unfavorable to the enrichment of lithium ion and Li^+ has difficulty enriching the higher concentration in the liquid phase, so when designing the actual production process, it should be considered to remove the sulfate in the early stage of evaporation; when the water loss rate is 68.76%, sodium chloride begins to saturate and precipitate. However, at this time, the sodium ion content does not decrease significantly. The reason is that the concentration of sodium ion in the middle and late stages of evaporation is already very high, and its precipitation and enrichment rate are basically equivalent when the water loss rate is 74.83%. the potassium salt saturated and precipitated. Then potassium mirabilite was mainly added, and the growth rate of potassium ion in the solution slowed; when the water loss rate was 75.98%, lithium salts were
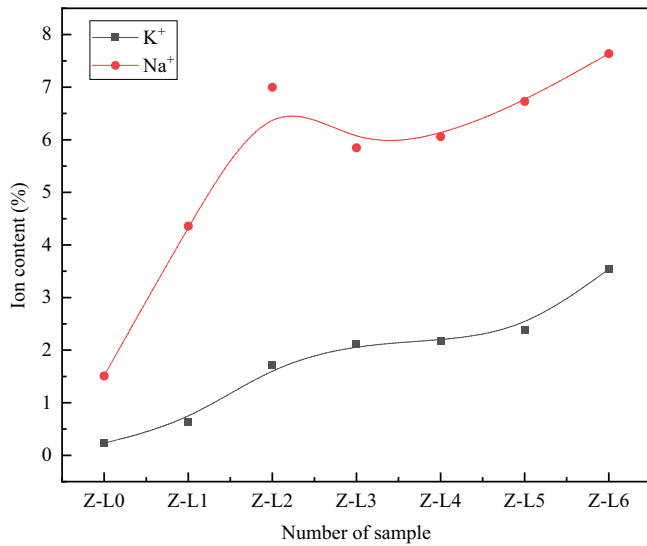

Fig. 2. Changes of K^+, Na^+ ions contents during 0°C isothermal evaporation of Lhaguo Tso Salt Lake.
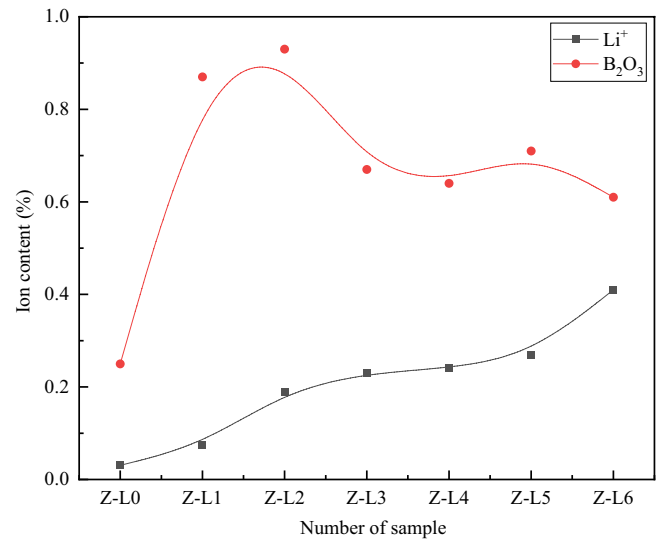

Fig. 3. Changes in Cl^- and SO_4^{2-} ions contents during 0°C isothermal evaporation of Lhaguo Tso Salt Lake.

Fig. 4. Changes of Li^+ and B_2O_3 ions contents during 0°C isothermal evaporation of Lhaguo Tso Salt Lake.
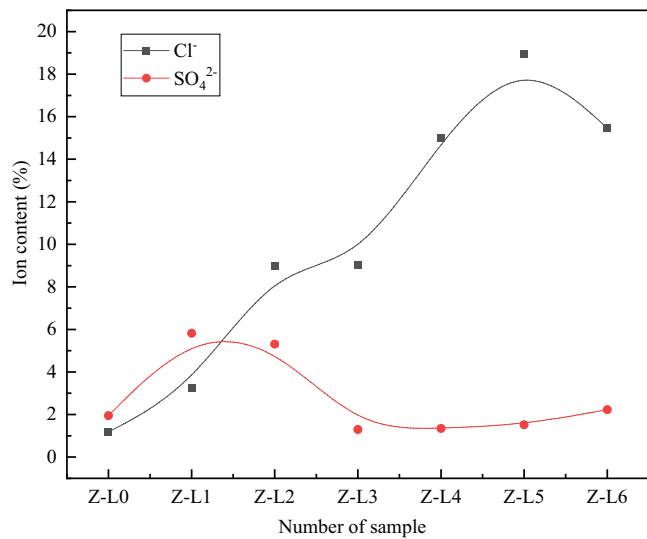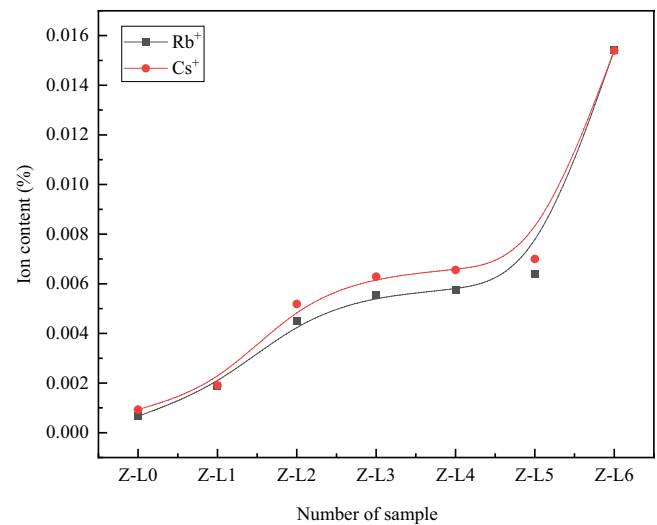

Fig. 5. Changes in Rb^+ and Cs^+ ions contents during 0°C isothermal evaporation of Lhaguo Tso Salt Lake.

saturated and precipitated by the forms of lithium potassium sulfate and lithium sodium potassium sulfate.

3.3. Enrichment rules of Li⁺ and B₂O₃ in the liquid phase during the isothermal evaporation of the brine from the Lhaguo Tso Salt Lake at 0°C

Table 6 and Fig. 3 show that the enrichment law of lithium and boron in the liquid phase during the isothermal evaporation of the brine from the Lhaguo Tso Salt Lake at 0°C.

From Table 5 and Fig. 6 it can be seen that the Li^+ content increased and the content of B_2O_3 did not change significantly when it increased to a certain extent. during the isothermal evaporation experiment at 0°C in Lhaguo Tso Salt Lake. The concentration rate of Li^+ is higher than that of B_2O_3. However, both are much lower than the brine concentration rate, especially in the late evaporation stage, which indicates that at the late evaporation stage. Salt minerals formed by Li^+ and B_2O_3 are precipitated. Moreover, mother liquor entrainment and associated precipitation are more serious, which leads to a decrease in the increase rate of Li^+ and B_2O_3 contents in the liquid phase. Especially for B_2O_3, the content change in the later period evaporation stage is small, indicating that the amount of borate precipitation is large in the early evaporation stage, and low temperature is conducive to the precipitation of borax. Therefore, it can be considered a process for separating and extracting boron.

In this paper, the experiment of 0°C isothermal evaporation of Lhaguo Tso Salt Lake was carried out, and the crystallization route and salt precipitation rule of isothermal evaporation at 0°C were obtained. The relationship between liquid Li^+, B_2O_3 and brine concentration ratio during isothermal evaporation at 0°C was obtained (Fig. 7). The results of the isothermal evaporation experiment at 0°C for the brine of Lhaguo Tso Salt Lake were analysed, and the following conclusions were drawn:

- The original composition of the brine of Lhaguo Tso Salt Lake is located in the mirabilite region of the 0°C isothermal phase diagram of the Li^+, Na^+, K^+//Cl^-, SO_4^{2-}-H_2O five-element system and the salt precipitation of the brine during isothermal evaporation at 0°C. The order is (1) Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + $Na_2B_4O_7 \cdot 10H_2O$; (2) $NaCl$ + KCl + $MgCO_3 \cdot 3H_2O$ + $Na_2B_4O_7 \cdot 10H_2O$; (3) $NaCl$ + KCl + $Na_2SO_4 \cdot 3K_2SO_4$; (4) $NaCl$ + KCl + $Li_2SO_4 \cdot K_2SO_4$; (5) $NaCl$ + KCl + $2Li_2SO_4 \cdot K_2SO_4 \cdot Na_2SO_4$. In addition to carbonate, mirabilite and borax are saturated and precipitated before sodium chloride, potassium salt is mainly precipitated in the form
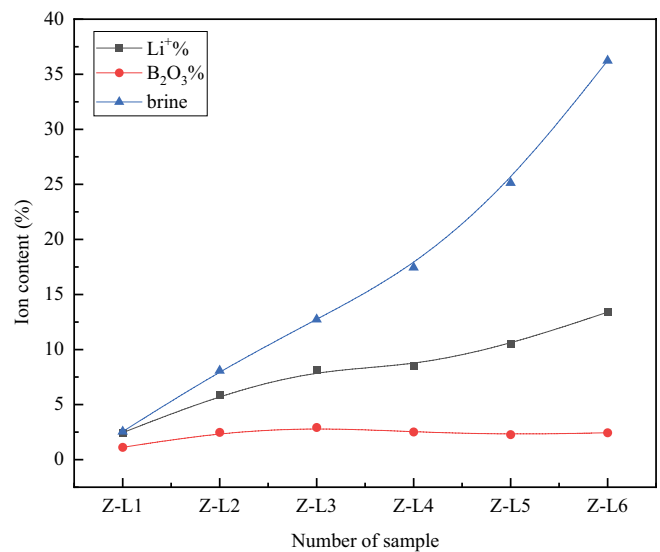

Fig. 6. Relationship between the concentration factor of brine and the enrichment factor of lithium and boron during the 0°C isothermal evaporation of Lhaguo Tso Salt Lake.

Table 6
Relationship between the concentration ratio of brine and the enrichment ratio of lithium and boron in the process of isothermal evaporation of brine from Lhaguo Tso Salt Lake at 0°C

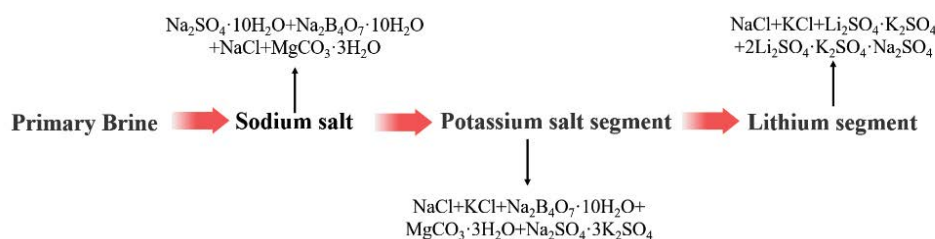| Numbering	Li^+% concentration multiple	B_2O_3% concentration multiple	Brine concentration multiple
Z-L1	2.45	1.12	2.55
Z-L2	5.88	2.48	8.08
Z-L3	8.17	2.92	12.74
Z-L4	8.50	2.52	17.45
Z-L5	10.46	2.28	25.13
Z-L6	13.40	2.44	36.23

Fig. 7. Isothermal evaporation and salt precipitation rules of Lhaguo Tso Salt Lake at 0°C

of potassium chloride and glaserite, and lithium salt is mainly precipitated in the form of lithium potassium sulfate and lithium sodium potassium sulfate.

- Borax is dispersed and precipitated during the isothermal evaporation of the brine in the Li-rich salt lake of Lhaguo Tso Salt Lake at 0°C, and sodium salt and potassium salt have been precipitated since precipitation.
- The isothermal evaporative crystallization route of Laguocuo Li-rich salt lake brine at 0°C is basically the same as the expression on the 0°C isothermal phase diagram of the Li$^+$, Na$^+$, K$^+$//Cl$^-$, SO$_4^{2-}$-H$_2$O five-element system.

3.4. Solubility prediction

Experimental study on the evaporation of salt lake brine is one of the indispensable and important processes for the development and utilization of salt lake resources. Evaporation experiments usually need to set a series of temperature conditions to more accurately simulate the actual environmental conditions of the salt lake so that the evaporation experiment results are more accurate and reliable, and provide a theoretical basis for the development and utilization of salt lake resources.

Evaporation experiments of brine are a process with complex conditions, long periods and heavy analyses. In many cases, experimental conditions are more limited. Therefore, people have been committed to the use of models to solve actual evaporation experimental research, and many scholars have carried out excellent research work. At present, the Debye–Hückel model [19], NRTL model [20], Pitzer model [21] and UNIQUAC model [22] are widely used, and each model has its own characteristics. In this paper, Lhaguo Tso Salt Lake Li-rich salt lake is an approximately Li$^+$, Na$^+$, K$^+$//Cl$^-$, SO$_4^{2-}$-H$_2$O five-element water-salt system, using the extended UNIQUAC model established by Thomsen. The principal equations of UNIQUAC model as follows [23]:

$$\frac{G_{\text{UNIQUAC}}^e}{RT} = \sum_i x_i \ln\left(\frac{\phi_i}{x_i}\right) - \frac{z}{2} \sum_i x_i q_i \ln\left(\frac{\phi_i}{\theta_i}\right) - \sum_i \left[x_i q_i \ln\left(\sum_j \theta_j \phi_{ij}\right) \right]$$ (1)

where z: coordination number, x_i: mole fraction, ϕ_i: volume fraction, and θ_i: surface area fraction.

Among them,

$$\phi_i = x_i r_i / \sum_j x_j y_j$$ (2)

$$\theta_i = x_i q_i / \sum_j x_j q_j$$ (3)

where r_i: volume parameter and q_i: surface area parameter.

The formula $\psi_{ij} = \exp\left(-\frac{u_{ji} - u_{ii}}{T}\right)$ can be used to calculate the interaction between substances. The interaction energy parameters are u_{ji} and u_{ii}, whose values are determined by a large number of experimental data.

In the process of calculating phase equilibrium, the minimum Gibbs free energy is used as the judgment basis. Firstly, the composition of the liquid phase with the lowest Gibbs free energy is obtained by phase equilibrium. Then, a possible solid precipitation is examined to see if it leads to a reduction in the Gibbs free energy of the system. If the phase equilibrium calculation results in a stable phase, the calculation stops. Otherwise, we continue to examine whether the Gibbs free energy will decrease if both salts are precipitated at the same time. Several salts may be supersaturated at the same time, and a combination of two supersaturated salts is used for equilibrium calculations until a solution is found. If there is no solution, simultaneous precipitation of 3 or more salts is required to obtain the lowest Gibbs free energy. The algorithm is fast when only one or two salts are precipitated at the same time. If more salt precipitates at the same time, the algorithm takes more time to solve. More details about this algorithm can be found in Thomsen's doctoral dissertation [24].

The simulation software AQSOL027 was used for theoretical simulation under the condition of 0°C. The software is based on Excel, and any temperature and system composition within the scope of the software are input after Gibbs free energy minimization calculation. The model outputs the equilibrium solution composition, the thermodynamic properties of the solution, the composition of the equilibrium solid phase and the mass of each solid phase.

The first part of the results is a statement on the speciation. The amounts of aqueous species are given in grams of each species. Next, the amounts of solids precipitated are stated. In the following rows, the "Saturation index before equilibrium" is given. Further down, "Saturation index after equilibrium" is given. The following is the detailed calculation process of the software (From the software manual).

The software consists of a 32-bit and 64-bit Dynamic Link Libraries and a Microsoft Excel Macro Enabled Workbook, AQSOL027.XLSM. The DLL files contain the Extended UNIQUAC thermodynamic routines required for equilibrium calculations in solutions with salts. The Microsoft Excel file contains various calculation examples that demonstrate how the DLL file can be called. The calculation examples in the Excel file are compared with experimental data from the open literature so that the accuracy of the calculations can be evaluated.

The AQSOL027.xlsm file contains the sheets "Props" and "Calculation". The "Calculation" sheet is meant as a template for performing calculations. You can make copies of the "Calculation" sheet and perform your calculations in these sheets. In the calculation sheet you can perform calculations for aqueous electrolyte solutions. The program accepts input in degree centigrade for the temperature and grams of each of the aqueous species. After you finish writing your input, you can right away read the results.

By comparing the experimental and calculated results on the phase diagram of the five-element system Li$^+$, Na$^+$, K$^+$//Cl$^-$, SO$_4^{2-}$-H$_2$O at 0°C [23], it can be seen that the trend of the calculated results is basically consistent with the trend of the experimental results, which meets the industrial requirements for the salt lake brine evaporation process. This shows that the UNIQUAC model is reliable in the evaporation process of brine in this kind of salt lake, as shown in Fig. 8.
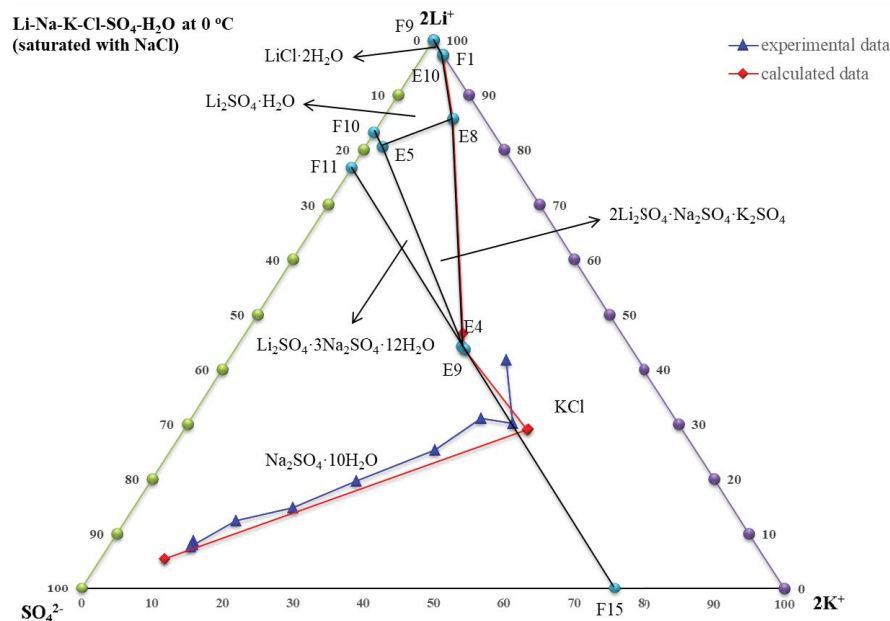
Fig. 8. Comparison results of experimental data and calculated data.

4. Conclusion

According to the characteristics of the chemical compositions of Lhaguo Tso Salt Lake, it can be judged that the original brine is carbonate saturated brine. As long as it evaporates, carbonate will be precipitated, but the amount of carbonate precipitated in the laboratory is relatively small. Especially in the early stage of evaporation, it can be ignored for the time being. Therefore, during the evaporation process, the brine of the Lhaguo Tso Salt Lake first passes through a large section of unsaturated salt mine (excluding carbonates) and then reaches the saturation point of glauber. Since the low temperature is conducive to the precipitation of mirabilite, and it is basically completed in the early and middle stages of evaporation, which can achieve the purpose of fully separating mirabilite. These results show that with the progress of the evaporation process, borax and mirabilite are precipitated together, the amount of carbonate precipitation increases from small to large, and the contents of both can be captured by XRD analyses. Then, there is saturated precipitation of sodium chloride, followed by the precipitation of potassium salt, and potassium salt is precipitated in the form of potassium chloride and potassium glauber. Finally, lithium salt precipitates in the form of lithium potassium sulfate ($Li_2SO_4 \cdot K_2SO_4$) and lithium sodium potassium sulfate ($2Li_2SO_4 \cdot K_2SO_4 \cdot Na_2SO_4$).

Acknowledgments

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