

Research Article

The Influence of the MRSP on the Freezing and Evaporation Processes of the Magnesium Sulfate Subtype Salt Lake Brine

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We have developed a new concept, which is the mass fraction ratio of sulfate and potassium ions (MRSP), for the magnesium sulfate subtype salt lake, which is calculated using the metastable phase diagram. We also studied the trend of the MRSP values with the temperature and the influence of the MRSP values on the evaporation process. The experimental results indicated that the MRSP value showed significantly negative trend with decrease of refrigerated temperature. Moreover, when the MRSP value of the objective brine is reduced to less than or equal to the *Specific Value* by freezing operation, the great changes of crystal morphology and stage of K^+ and SO_4^{2-} will take place, which makes the sequence of salts precipitation of the freezing-evaporation different from the direct-evaporation.

1. Introduction

Saline lakes are important mineral resources for national economy. China is famous for its large quantity, variety, and abundant rare elements of salt lakes [1]. Generally, according to the major elements compositions, the salt lake can be classified into five (or six) categories, that is, chloride type, sulfate type (includes magnesium sulfate subtype and sodium sulfate subtype), nitrite type, carbonate type, and borate type [2]. For magnesium sulfate subtype salt lake, depending on the proportion of SO_4^{2-} , the composition point of original brine always located in astrakhanite, schoenite, or sylvite region in the metastable phase diagram (MPD) of Na^+ , K^+ , Mg^{2+}/Cl^- , and SO_4^{2-}/H_2O at 25°C [3]. As a result, the varied double salts will precipitate during evaporation process of such salt lake brine [4]. For example, the potassium ions will precipitate in the form of schoenite, sylvite, and carnallite when the composition point is located in the schoenite region [5–7]. If the potash-bearing salts mixtures were used to produce potash fertilizer as raw materials, the process would be rather complex and the low yield of potassium ion would be obtained. Then, the diversified precipitations have unfavorable effect on the comprehensive utilization [8].

One way to solve this problem is freezing. The studies of brine freezing usually focus on precipitation pathway at subzero temperatures [9–11] and the desalination by freezing [12–16]. There is a potential application prospect of freezing desalination for salt lakes because saline lakes are generally distributed in high altitude and arid region with low temperature in winter.

Although previous studies indicated that the composition and crystallization paths could be optimized by means of freezing operation [17, 18], there are no effective methods to calculate and judge the degree of freezing operation.

This paper aims to explore the influences on the evaporative crystallization process for magnesium sulfate subtype brine by using freezing operation. A new concept, called the mass fraction ratio of sulfate and potassium ions (MRSP), was developed, which can be used to judge the degree of brine freezing. The results showed that the MRSP value had dropped from 7.93 to 3.46 when the brine was cooled from room temperature to -5°C . The astrakhanite and schoenite phase disappeared in the process of evaporative after being frozen, and the potassium ion precipitated in the form of sylvite and carnallite. Therefore, the suitable raw materials with the enhancement of the yield for potassium sulfate can be obtained. The results also demonstrated that the

TABLE 1: Main chemical composition of the studied brine.

Sample number	Density g·cm ⁻³	Chemical composition%								
		K ⁺	Na ⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	Li ⁺	CO ₃ ²⁻	HCO ₃ ⁻	
L0	Original brine	1.285	1.07	5.96	2.78	12.16	8.55	0.0081	0.17	0.051

TABLE 2: Ionic composition (%) of the studied brine samples, measured at different temperatures, and the index of phase diagram.

Sample number	Refrigerated temperature °C	Chemical composition%					Index of phase diagram		
		K ⁺	Na ⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	2K	Mg	SO ₄
L1	-18.0	1.48	3.14	3.71	16.05	1.55	9.05	83.24	7.71
L2	-13.0	1.44	3.36	3.70	15.94	1.65	8.80	82.99	8.21
L3	-5.0	1.30	4.40	3.34	14.20	4.20	7.66	72.21	20.14

precipitation sequences of original and frozen brine were in accordance with MPD at 25°C.

2. Materials and Methodology

Brine samples for the experiments were collected from a typical magnesium sulfate subtype salt lake from Qaidam Basin of China in summer. The major ionic chemical composition of the original brine is given in Table 1.

Na⁺, K⁺, Mg²⁺, Cl⁻, and SO₄²⁻ ions together contribute 99 wt% of the total. The MPD for the quinary system of Na⁺, K⁺, Mg²⁺, Cl⁻, and SO₄²⁻-H₂O can be suitable for predicting and explaining the concentration and crystallization behaviors of major elements in the objective brine [19].

This study includes freezing process and isothermal evaporation. For the freezing treatment, an enamel pail accompanied with original brines (2.00 Kg) was stored in a refrigerating cabinet without stirring. The brine was cooled from ambient temperature to the setting subzero temperature and maintained for at least 24 hours. The solid was separated from the bittern quickly when the precipitation occurred. Besides, the samples were collected at subzero temperature. However, it is important to point out that the chemical analysis was conducted at ambient temperature.

The isothermal evaporation experiment was carried out in the lab. Concretely, the objective brine was stored in a plastic basin and in the meantime the brine temperature was regulated at 25°C by a mercury contact thermometer. An incandescent lamp was used to supply continuous heat and an electric fan was used as an air draft source. The new precipitation was taken three times per day, then examined, and analyzed by the polarizing microscope to identify the minerals phase. The solid and liquid phases should be separated when a new mineral phase precipitation occurred, and the relevant parameters such as complete chemical analysis of solid and liquid phases were then determined.

The following analytical methods were used [20]: K⁺ and Na⁺ were determined by flame atomic absorption spectrometry. Mg²⁺ was determined by complexometric titration with EDTA. SO₄²⁻ was determined by barium sulfate gravimetric method and Cl⁻ was analyzed by silver nitrate volumetric titration.

TABLE 3: Solid phase appearing in the phase diagram at 25°C involving the systems Na⁺, K⁺, Mg²⁺/Cl⁻, and SO₄²⁻//H₂O with halite saturation throughout.

Abbreviation	Salt mineral	Chemical formula
Mir	Mirabilite	Na ₂ SO ₄ ·10H ₂ O
Gla	Glaserite	Na ₂ SO ₄ ·3K ₂ SO ₄
Sy	Sylvite	KCl
Pic	Schoenite	K ₂ SO ₄ ·MgSO ₄ ·6H ₂ O
Ast	Astrakhanite	Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O
Eps	Epsomite	MgSO ₄ ·7H ₂ O
Car	Carnallite	KCl·MgCl ₂ ·6H ₂ O

3. Results and Discussion

3.1. Freezing at Different Subzero Temperatures and Prediction of the Crystallization. During the experimental freezing progress, the original brine was refrigerated at -18°C, -13°C, and -5°C, respectively. The analysis results for major ions of the studied brine at various temperatures are given in Table 2. The mineral salts involved in the diagram are summarized in Table 3. And the phase diagram points were drawn in the MPD of Na⁺, K⁺, Mg²⁺/Cl⁻, and SO₄²⁻//H₂O at 25°C (Figure 1).

In Table 2 and Figure 1, the mass fraction of SO₄ in brine decreased significantly as the temperature decreased, and the composition points of the liquid are all located on a straight line, extended from the tie line of the original brine composition point and the original point of SO₄ on the triangular phase diagram. L0 is located in the astrakhanite region; L3 is located in epsomite region while L2 and L1 move to sylvite region. Then, the crystallization pathway of such kind of brines (L0~L4) can be predicted by using the location of coordinates on the MPD. Accordingly, if the solution reached the bischofite saturated point, the predicted precipitation should be present in sequences as in Table 4. It is assumed that the brine position remains constant during halite crystallization until the potash and magnesium sulfate bearing salts precipitation occur.

From Table 4, the kinds of predicted minerals of original brine (L0) were much more than L1, L2, and L3. Apparently, compared with L1, the astrakhanite and schoenite phases

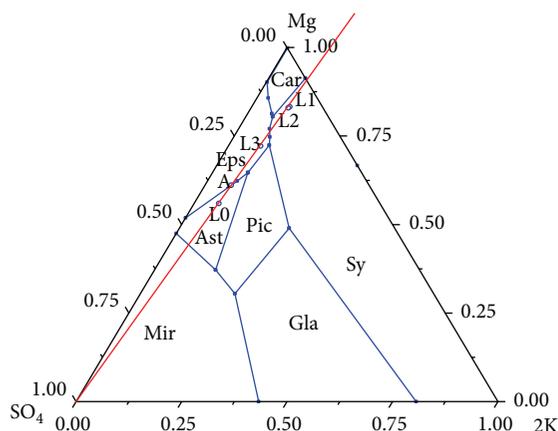


FIGURE 1: Location of the studied initial brine and liquid phase at different temperatures on the phase diagram at 25°C involving the system Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, and $\text{SO}_4^{2-}/\text{H}_2\text{O}$ with halite saturation throughout.

TABLE 4: The predicted sequences of the crystallization.

L0	L1 and L2	L3
Halite		
Halite + Ast	Halite	Halite
Halite + Pic + Eps	Halite + Sy	Halite + Eps
Halite + Sy + Eps	Halite + Car	Halite + Sy + Eps
Halite + Car + Eps	Halite + Car + Eps	Halite + Car + Eps

TABLE 5: The MRSP of L0~L3.

Brine number	Temperature	MRSP
L0	Ambient	7.99
L1	-18.0°C	1.05
L2	-13.0°C	1.15
L3	-5.0°C	3.23

were absent in the sequence of L3, and potassium ion precipitated in the type of carnallite with epsomite in the later carnallite stage in the sequence of L1 and L2 because of the frozen operation.

From the conclusions we draw here, it is clear that temperature has a remarkable effect on the mass fraction of SO_4^{2-} in the brine; meanwhile, the mass fraction of SO_4^{2-} may have great influence on the distribution and crystal morphology of K^+ in the process of crystallization of salts. Therefore, the new concept of MRSP was developed, which can be used to describe the relationship between K^+ and SO_4^{2-} .

3.2. Concept of MRSP. MRSP can be calculated by

$$\text{MRSP} = \frac{\text{SO}_4\%}{\text{K}\%}. \quad (1)$$

The MRSP of L0~L3 are listed in Table 5.

From Table 5 and Figure 1, we can see that the value of MRSP starts to decline from 7.99 at ambient temperature to

TABLE 6: The chemical composition of the liquid phase formed by 25°C-isothermal direct- and freezing-evaporation of brines.

Sample number	Density $\text{g}\cdot\text{cm}^{-3}$	Chemical composition%						MRSP
		K^+	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	H_2O	
D-L0	1.285	1.07	5.96	2.78	12.16	8.55	69.47	7.99
D-L1	1.298	1.25	5.75	3.17	12.33	9.34	68.15	7.47
D-L2	1.306	1.88	3.99	4.21	13.32	8.72	67.87	4.64
D-L3	1.309	2.09	3.31	4.48	13.76	8.07	68.27	3.86
D-L4	1.328	2.33	1.63	5.92	15.69	7.05	67.36	3.03
D-L5	1.322	2.18	1.47	5.77	16.76	5.30	68.49	2.43
D-L6	1.334	1.80	0.78	6.63	18.66	5.06	67.03	2.81
D-L7	1.335	0.71	0.43	7.48	19.85	3.94	67.55	5.55
D-L8	1.365	0.19	0.22	8.61	22.23	3.41	65.28	17.95
F-L0	1.285	1.09	6.10	2.80	12.18	8.64	69.18	7.93
F-L1	1.257	1.32	4.54	3.48	14.60	4.57	71.48	3.46
F-L2	1.296	1.90	2.70	4.75	14.86	6.50	69.28	3.42
F-L3	1.322	2.26	1.32	6.03	16.97	5.52	67.88	2.44
F-L4	1.331	1.10	0.62	6.89	18.68	3.86	68.82	3.51
F-L5	1.370	0.11	0.19	8.62	22.50	2.92	65.61	26.55

1.05 at -18.0°C. Accordingly, the composition point moves to sylvite region from astrakhanite region across the epsomite (L0→L1). Meanwhile, the kind of sulfates salts has been cut down in the predicted crystallization sequence; it is the absence of astrakhanite and picromerite. Hence, there should be a *Specific MRSP* value here. If the MRSP of the objective brine is greater than *Specific MRSP*, the brine should be frozen at subzero temperature to ensure that the MRSP should be less than the *Specific MRSP*. Actually, the *Specific MRSP* can be obtained by means of MPD of the Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, and $\text{SO}_4^{2-}/\text{H}_2\text{O}$. For example, in this study, through the analysis for phase diagram, a straight line connected the composition points of the original brine and the original point of SO_4 cut the cosaturation line of astrakhanite and epsomite at point A (shown in Figure 1), in which the calculated MRSP value is 6.48. Therefore, the 6.48 value should be the *Specific MRSP* value for the studied brine. In other words, the MRSP of studied brine should be less than or equal to 6.48 by freezing methods.

3.3. Crystallized Sequences of Direct- and Freezing-Evaporation. To observe the changes of crystallization pathway of salt minerals after the MRSP was reduced, the direct-evaporation and freezing-evaporation experiments were carried out. The results including chemical composition of liquid and solid phase at 25°C are detailed in Table 6. The crystallization pathway of brine at 25°C is shown in the quinary system phase diagram of Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, and $\text{SO}_4^{2-}/\text{H}_2\text{O}$ at 25°C (Figure 2).

There are seven solid phase regions saturated with NaCl, including mirabilite, glaserite, sylvite, schoenite, astrakhanite, epsomite, and carnallite.

For the direct-evaporation experiment, the composition point of the objective original brine at 25°C is located in the

TABLE 7: Composition of compounds for direct-evaporation crystallization.

Stage	Compounds composition%							Distribution of K ⁺ %
	NaCl	KCl	MgCl ₂	Na ₂ SO ₄	MgSO ₄	K ₂ SO ₄	H ₂ O	
Halite	62.57	—	—	8.83	9.71	0.76	18.13	1.06
Ast	43.20	—	—	17.87	20.11	0.71	18.10	4.43
Mixed potassium								
Pic	33.51	—	—	—	26.45	5.75	33.29	38.89
Sy	27.29	17.58	3.98	—	21.23	—	29.92	18.45
Car	8.39	15.88	17.49	—	20.64	—	37.60	34.59

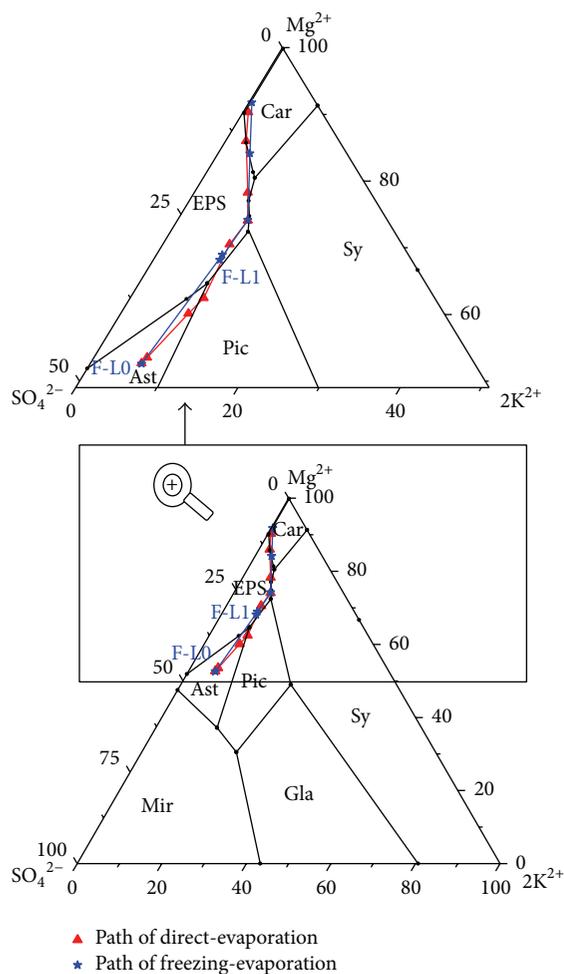


FIGURE 2: Graphical representations of the evaporation pathway on the MPD at 25°C showing (red triangle) direct-evaporation crystallization and (blue star) freezing-evaporation crystallization.

astrakhanite region. Because most of the salts are NaCl, halite crystallized immediately after the beginning of isothermal evaporation. The second salt that precipitated is astrakhanite. The composition point of the liquid phase mainly follows the path from the original brine composition point to the astrakhanite solid phase point, where halite and astrakhanite are the principal precipitated salts, then followed by schoenite together with halite and epsomite. Hence, sylvite saturation is achieved, and the precipitation processes of sylvite and

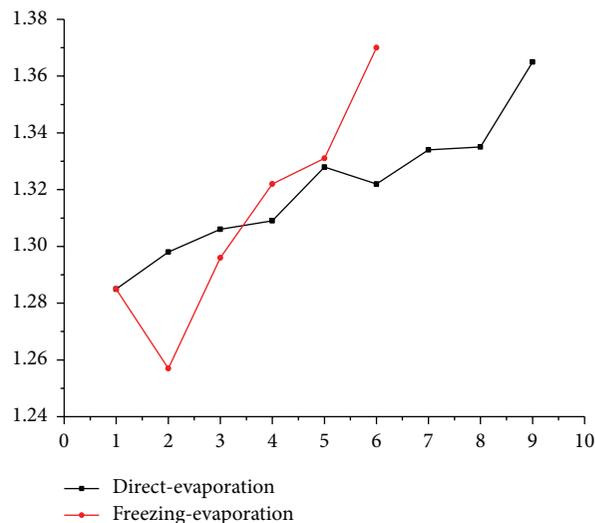


FIGURE 3: The changing trend of density in the process of two evaporations.

epsomite have been accomplished. Large amounts of carnalite start to precipitate with some epsomite during the late period of experiment. The sequence of mineral precipitation from the brine at 25°C is in accordance with the summary listed in Table 3.

For the freezing-evaporation experiment, the original brine composition point moves to epsomite from astrakhanite region (F-L0 to F-L1), and the MRSP value has dropped from 7.93 to 3.46 (less than the *Specific* MRSP value 6.48) after freezing at -5°C. The second saturated and precipitated salt is epsomite instead of astrakhanite. The pathway of freezing-evaporation is the same with the direct-evaporation pathway after the saturation of sylvite.

The results also show that both the precipitation sequences are in good agreement with MPD at 25°C.

Based on the results of our experiments, the entire evaporation process could be divided into five basic stages and composition of compounds are listed in Tables 7 and 8, respectively, for direct-evaporation and freezing-evaporation crystallization (composition of compounds is ore matching based on the ion analysis results).

According to the data in Tables 7 and 8, the difference in compounds composition between the direct-evaporation and freezing-evaporation experiments lies in the crystallization

TABLE 8: Composition of compounds for freezing-evaporation crystallization.

Stage	Compounds composition%							Distribution of K ⁺ %
	NaCl	KCl	MgCl ₂	Na ₂ SO ₄	MgSO ₄	K ₂ SO ₄	H ₂ O	
Mir	2.80	—	—	37.86	1.88	0.31	57.15	2.28
Halite	92.02	0.46	1.04	—	0.86	—	5.62	1.33
Mixed potassium								
Eps	35.46	5.43	1.67	—	25.19	—	32.25	19.29
Sy	11.13	14.70	13.04	—	21.21	—	39.90	49.34
Car	7.17	11.92	24.05	—	12.44	—	44.37	24.71

type and stage of K⁺ and SO₄²⁻. For the direct-evaporation, the distribution of potassium ion in picromerite, sylvine, and carnallite stages was about 91.93%. That is to say, most of the potassium ions precipitated in the forms of K₂SO₄·MgSO₄·6H₂O, KCl, and KCl·MgCl₂·6H₂O. On the other hand, SO₄²⁻ always precipitated in the different forms of double salts at different stages, such as double salts Na₂SO₄ and MgSO₄ at the astrakhanite stage, double salts K₂SO₄ and MgSO₄ when the picromerite is saturated, or epsomite at the sylvite and carnallite stage.

For the freezing-evaporation, a large amount of SO₄²⁻ precipitated at the low temperature in the freezing mirabilite stage, and some SO₄²⁻ in the residual brine precipitated in the form of mirabilite and double salt or hydrated salt of magnesium sulfate through the evaporation process. K⁺ precipitated only in the form of KCl over the entire isothermal evaporation process.

Through the comparative analysis of the two tables, we can find that the crystallization type and stage of K⁺ and SO₄²⁻ have changed significantly with the decrease of MRSP value. Therefore, the MRSP will be an important parameter, which can be used to estimate the composition of the salt lake brine.

3.4. Trend of the Density. Figure 3 presents the changing trend of density in the process of two evaporations. For freezing-evaporation, as the program went on, the density increased initially and then reduced. And for direct-freezing, the density increased from beginning to end. The variational trend was also found in MRSP value.

4. Conclusions

The following conclusions are drawn based on the experiments at subzero temperature and 25°C. The content of SO₄²⁻ in brines has decreasing trend with the decreasing of temperature; in other words, the MRSP was decreased. The *Specific Value* of MRSP can be calculated using the composition point coordinates and the metastable phase diagram relating to the Na⁺, K⁺, Mg²⁺, Cl⁻, SO₄²⁻, and H₂O system. If the MRSP in the objective brine is higher than *Specific Value*, the brine should be frozen at subzero temperature to ensure that the MRSP keeps less than the *Specific Value*. Both predicted and experimental sequences of the evaporation process demonstrated that the great changes of crystal morphology and stage of K⁺ and SO₄²⁻ had taken

place after the decrease of MRSP. As a concrete manifestation of the absence of astrakhanite and picromerite minerals and the simplification of K⁺ crystallized forms and so forth, the MRSP thus would be important reference information to judge the composition of the brine for the comprehensive utilization.

Additional Points

Highlights. (1) Put forward a new concept MRSP and *Specific MRSP* and present the calculating methods using the metastable phase diagram. (2) The trend of the MRSP values with the decreasing temperature and the influence of the decreased MRSP values on the evaporation process were studied. (3) The differences of crystal morphology and stage of K⁺ and SO₄²⁻ were described between the conditions of the MRSP value which was decreased and not.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this article.

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