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Solubility Property of Brine with Different Dilutions Ratio and Properties Analysis of Low-Grade Solid Potash Ores

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Abstract. In this paper, the physical properties of brine with different dilution ratio, such as density, pH value, viscosity, electrical conductivity and refractive index were studied. Meanwhile, the solubility property of sodium chloride (NaCl), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and potassium chloride(KCl) in the dilution brine at different temperature were investigated. All of physical properties of brine with different dilutions regular changes were showed. Following with the elevating of the mass ratios, the increasing rate of the solubility of NaCl, $MgCl_2 \cdot 6H_2O$ and KCl tends to be reduced. And the solubility of chloride-type inorganic salts increased when added the dilution ratios of brine at different temperatures. The solubility in brine is strongly dependent on the presence of other ions in solvents. The differences in the solubility might strongly influence the physical and chemical property of the brine in dissolution of low-grade potassium deposit. We used the XRD analysis method and SEM analysis the typical particles to get in-depth understanding the occurrence characteristics of low-grade sulfate type solid potash ores in Dalangtan area of China. These basic data which was useful for extracting potassium chloride (KCl) from chloride-type brine was consummated.

Keywords: Physical properties, brine, solubility, magnesium chloride

1. Introduction

Salt lakes are widely distributed in the northwest of China. To illustrate, some lakes in the Qinghai-Xizang (Tibet) Plateau have the greatest concentration of the salt in China. Situated in the northwest of Qinghai province in China, Caidamu Basin which is known as the Chinese cornucopia consists of a series of saline lakes, such as Caerhan Lake, Dongtai Lake, Xitai Lake and Yiliping Lake. Among these lakes, Caerhan Lake is the main source of Chinese potassium fertilizer. The natural brine of this area is highly similar to the seawater system($Na+K+Mg+Cl+SO_4+H_2O$) [1]-[3].

There exists a big gap in the utilization of potash fertilizers in the large agricultural country, China [4]-[6]. Nevertheless, numerous salt lakes with Potash resources contribute to help alleviate the national shortage of potash fertilizers to some extent, which, however, fail to meet China's great demand for potash resources. As a result, 70% of the potash consumption remains dependent on import [7]-[9]. The main characteristic of solid potassium deposit in China is less high-grade potassium deposit and more low-grade solid potassium deposit. As yet, numbers of low-grade solid potassium deposit has not been made comprehensive use. Brine is the kinds of complex solutions which contains many ions such as Mg^{2+}, K^+, Na^+, SO_4^{2+}, Cl^- and a little of some other ions. It is one of the industrial scrap from factories near salt lakes, which can influence the surrounding environment if it is directly discharged [10]-[12]. To extend the service life of salt lake and get full use of low-grade solid potassium deposit, we study the dissolution low-grade solid potassium deposit technique.

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We want to dissolve the low-grade solid potassium deposit in diluted brine. It's known by X-ray diffraction that the low-grade solid potassium deposit in Dalangtan area contains NaCl, KCl and MgCl $6H_2O$.

So it is necessary to study solubility of NaCl, KCl and MgCl $6H_2O$ in diluted brine [13]-[16].

In this article, the physical properties of brine with different dilution ratio, such as density, pH value, viscosity, electrical conductivity and refractive index were studied. We used the brine from Liangzhong deposit of Dalangtan Basin in Chinese as one material of solvents. Meanwhile, the solubility property of sodium chloride (NaCl), magnesium chloride ($MgCl_2$ $6H_2O$) and potassium chloride (KCl) in the dilution brine at different temperature were investigated. Using the brine as material can help us carry out extract potassium chloride (KCl) from chloride-type brine.

2. Experimental Section

2.1. Apparatus and reagents

Doubly deionized water (DDW) with conductivity less than 10^{-4} S m^{-1} and pH 6.6 at room temperature (298.15 K) was used to dilute the brine and for chemical analysis. The purity grade of the reagent NaCl is greater than 99.5 mass%. And this reagent was obtained from Tianjin Dengke Chemical Reagent Ltd. A DF-101S heat collection-constant temperature type magnetic stirrer with a precision of ±1 K was designed by Changzhou National Laboratory Equipment Research Institute for solubility experiments. A gravity bottle method with a precision of ±0.0002 g cm^{-3} was used for the determination of the density of the original brine and the diluted brine. The original brine was collected in the salt lake of Liangzhong deposit of Dalangtan. X-ray diffraction was used to analyze the composition of low-grade solid potassium deposit in Dalangtan area.

The magnesium sulfate subtypes brine was collected from Dalantan salt lakes in summer, belonging to Qinghai Mangai Xingyuan Potash Limited Liability Company. Raw brine ions compositions by chemical titration analysis were showed in Table 1.

Table 1: The ions composition of the magnesium sulfate subtypes brine from low-grade potash ores.

Inorganic ions	Na^+	K^+	Mg^{2+}	Cl^-	SO_4^{2-}
Percentages (wt%)	1.83	1.54	5.30	16.19	4.69

2.2. Experimental method

The in-situ sampling method was used in this study to decrease the system error. A series of new solvents were mixtures of the original brine and DDW using different mass ratios. The water/brine mass ratios used were 0, 0.5, 1.0, 1.5, 2, 2.5, and 3.0 showed in Fig.1 respectively. During the dissolution experiments, the quantity of NaCl is excessive and loaded into a clean glass container. Then the solvent with the mass ratio of 1:0.5 was added into the container, and the container was put into the DF-101S heat collection-constant temperature type magnetic stirrer at 293.15(±1)K. After the whole system being stirred well for two hours, 2ml supernatant was quickly transferred into volumetric flask to analyze the concentration of Cl^- ion. Meanwhile, adding DDW into the container to change the mass ratio of the original brine and DDW into 1:1. The next step is as the same as the above description. We didn't change the temperature until the mass ratio of the original brine and DDW in the solvent had become 1:3 and 2ml supernatant had been transferred. We also studied the dissolution property of NaCl in solvents with different mass ratios of the original brine and DDW at 308.15(±1) K, 328.15(±1) K, 348.15(±1) K, 358.15(±1) K.

2.3. Testing method

The quantitative analyses of brine ions compositions were: the sodiumc tetraphenylborate-quaternary ammonium salt reversed titration method to determine the concentration of K^+[9], EDTA titration determination of Mg^{2+} content; Mercury method to determine the Cl^- content; $BaCl_2$ turbidity method to determine the SO_4^{2-} content and Na^+ ion content measured using equivalent minus according to ion balance.

3. Result and Discussion

Densities of the original brine and the diluted brine at 298.15K were determined and are showed in Fig. 1. These data are useful for calculation of the solubility of sodium chloride. Fig. 2 is XRD image of low-grade solid potassium deposit, It is shown that the low-grade solid potassium deposit in Dalangtan area contains NaCl, KCl and $MgSO_4•6H_2O$. Fig. 3 is SEM of low-grade solid potassium of magnesium sulfate subtypes. The results showed the potassium chloride amongst sodium chloride substrate with each other associated. Fig. 2 (F) was the horizontal cross section graph of low-grade solid potassium deposit. The others physical properties of brine with different dilution ratio, such as pH value, viscosity, electrical conductivity and refractive index were showed in Fig.4-7. These works have some reference significance for the comprehensive utilization of low grade sulfate type solid potash ores.

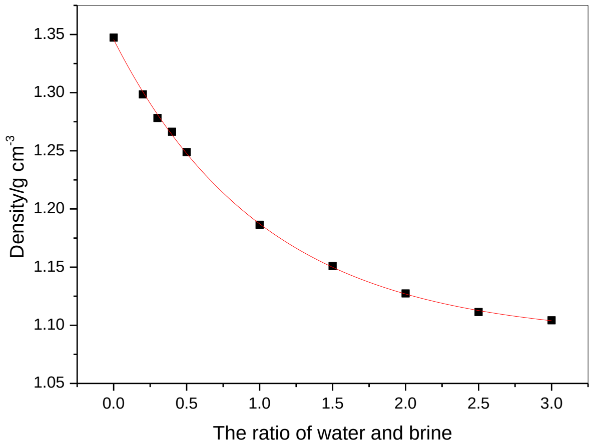

Fig. 1: The density of the brine of different dilution ratio

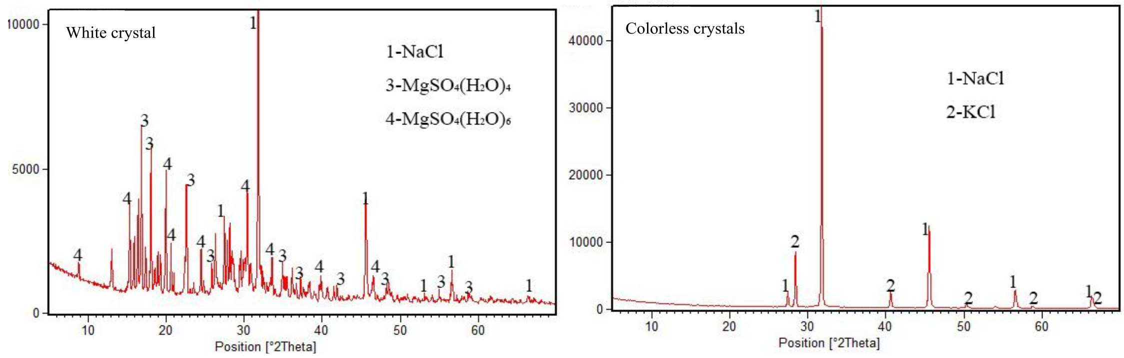

Fig. 2: XRD image of different crystalline low-grade solid potassium deposit

Will wave beach area extracting potassium old bittern using diluted with water to its solvent on the basis of physical properties were determined. The density, pH value, viscosity, conductivity and other physical parameters along with the change of dilution ratio curve. The physical parameters of the measurement for the actual deployment of old bittern provide the basis data used for dissolving ore process, is helpful to choose appropriate leaching conditions.

The effect of the mass ratios of doubly deionized water and the original brine on the solubility of magnesium chloride hexahydrate at different temperatures was investigated and the result show in Fig.7. From this result, we can see that the solubility of magnesium chloride hexahydrate increased when the mass ratios of DDW and the brine increased. While the increasing rate of the solubility of magnesium chloride hexahydrate tends to be reduced following with the elevating of the mass ratios of DDW and the brine. These results were caused by the influence of salting-out effect weakened because of the decrease in the concentrations of all the ions in solvents [17]-[20].

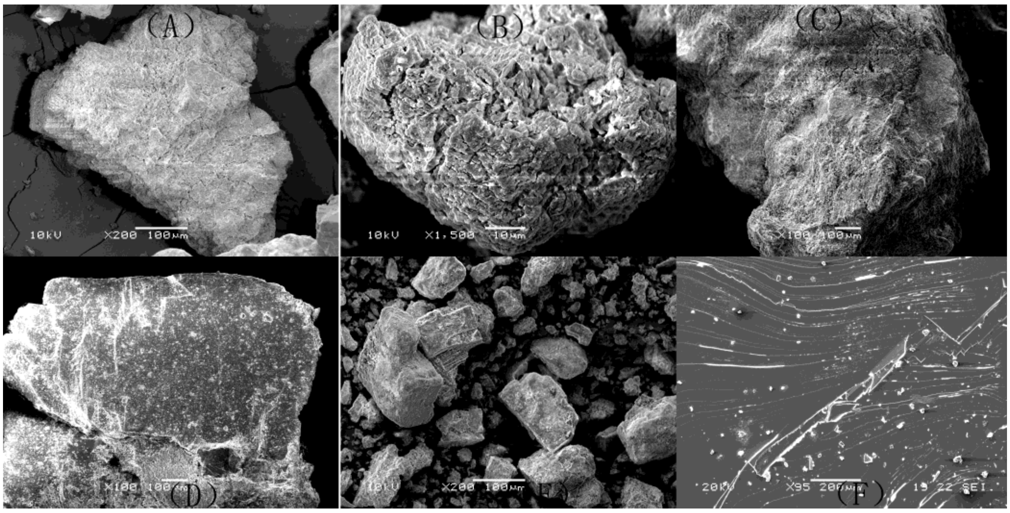

Fig. 3: SEM image of low-grade solid potassium of magnesium sulfate subtypes

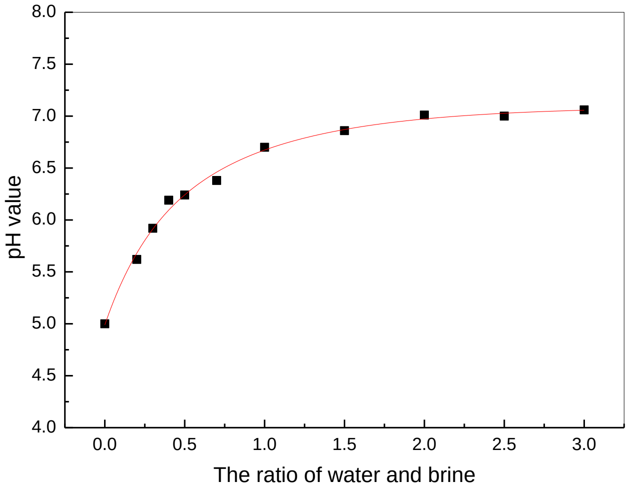

Fig. 4: pH value of the brine of different dilution ratio

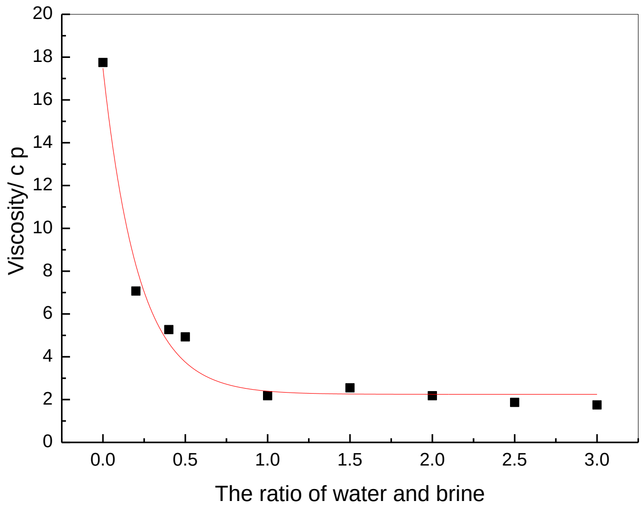

Fig. 5: The viscosity of the brine of different dilution ratio

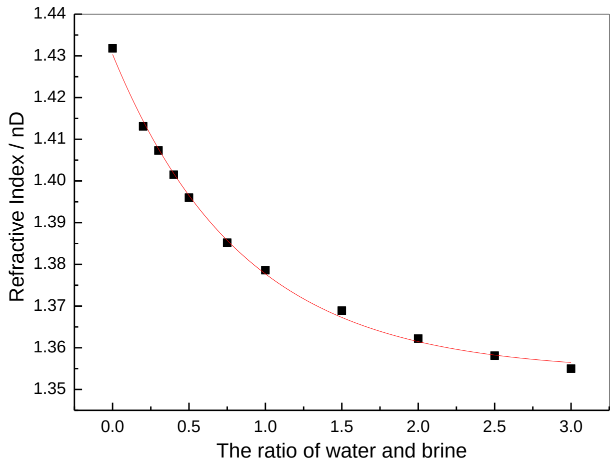

Fig. 6: The refractive index of the brine of different dilution ratio

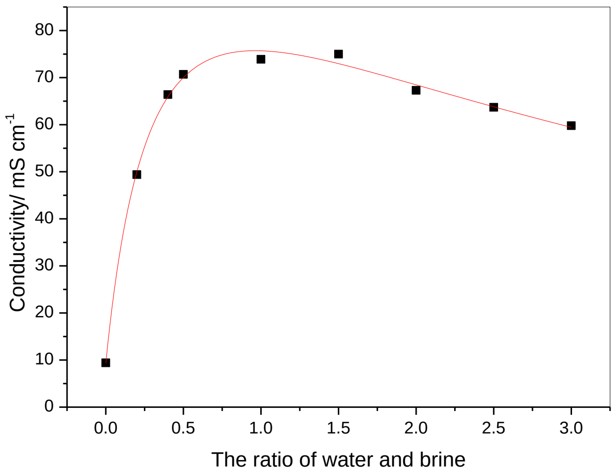

Fig. 7: The conductivity of the brine of different dilution ratio

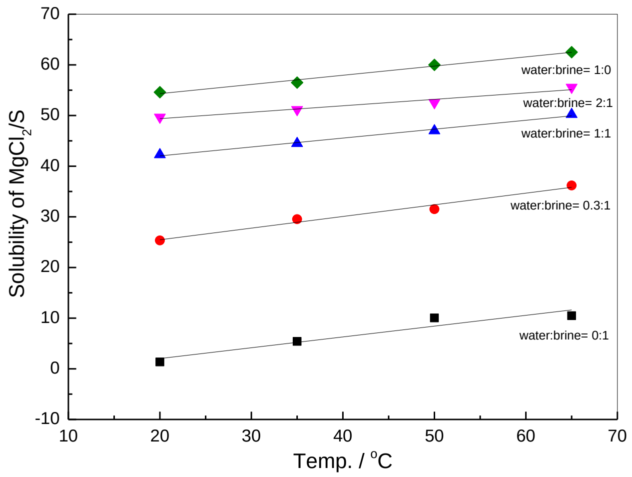

Fig. 8: The solubility of magnesium chloride hexahydrate under the different temperature

We can get from Fig. 8 that the increasing of temperature showed little influence on the solubility of magnesium chloride hexahydrate in diluted brine just like in pure water. That may be because ions in solvent moved quickly with the increasing of temperature, which had little effect on the solubility of sodium chloride. It was also found that the solubility of magnesium chloride hexahydrate in pure water was much higher than ones in diluted brine because of salting-out effect [21], [22]. In other words, the solubility of magnesium chloride hexahydrate in brine is the result of the common effect of all those ions in brine.

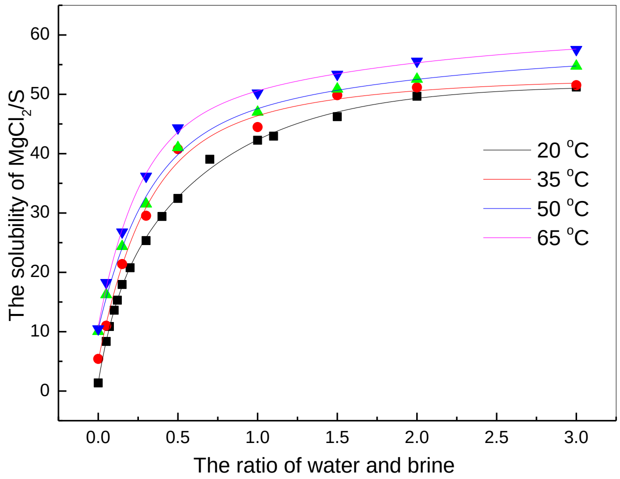

Fig. 9: The solubility of magnesium chloride hexahydrate of under different dilution ratios of old bittern

Fig. 9 showed that the solubility of $MgCl_2$ $6H_2O$ in K^+, Na^+, Mg^{2+}//Cl^-, SO_4^{2-}—H_2O brines has been measured in the temperature range of 20 to 65 C using the isothermal dissolution method. The solubility of $MgCl_2$ $6H_2O$ in all cases investigated was found to decrease with increasing temperature. Meanwhile, we ignored the change of volume in liquid phase during the process of calculation. according to the equilibrium phase diagram of the quinary system K^+, Na^+, Mg^{2+}//Cl^-, SO_4^{2-}—H_2O [23], [24].

In order to study the effects of ions on the solubility of magnesium chloride hexahydrate, we need to know the solubility varying with the mass-ration of ions in brine. But there are complex interactions between ions; the effect of ions on the solubility of magnesium chloride hexahydrate in brine need further study. And this is our next work.

4. Conclusion

In order to get full use of low-grade solid potassium deposit and study the solubility of compositions of low-grade solid potassium deposit in diluted brine. In this paper, the physical properties of brine with different dilution ratio, such as density, pH value, viscosity, electrical conductivity and refractive index were studied. All of physical properties of brine with different dilutions regular changes were showed. Following with the elevating of the mass ratios, the increasing rate of the solubility of NaCl, $MgCl_2$ $6H_2O$ and KCl tends to be reduced. And the solubility of chloride-type inorganic salts increased when added the dilution ratios of brine at different temperatures. The solubility in brine is strongly dependent on the presence of other ions in solvents. The differences in the solubility might strongly influence the physical and chemical property of the brine in dissolution of low-grade potassium deposit. We used the XRD analysis method and SEM analysis the typical particles to get in-depth understanding the occurrence characteristics of low-grade sulfate type solid potash ores in Dalangtan area of China. These basic data which was useful for extracting potassium chloride (KCl) from chloride-type brine was consummated.

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6. References

[1] Y. F. Guo, H. J. Yin, X. H Wu, T. L Deng. Metastable phase equilibrium in the aqueous auaternary system ($NaCl$+$MgCl_2$+Na_2SO_4 +$MgSO_4$ +H_2O) at 323.15 K, *J. Chem. Eng. Data*, 2010, 55: 4216-4220.

[2] D. G. Liu, J. Q. Chen, C. M. Zhang. The types and hydrochemical characters of salt lakes in chaidamud basin, *J. Salt Lake Res.*, 1996, 4 (3-4): 9-19.

[3] W. H. Cao, C. Wu. Brine resources and their comprehensive utilization technology, *Geol. Publishing House:*

Beijing, 2004, 87-177.

[4] M. L. Wang, Y. J. Wang, C. L. Liu, Y. Z. Chen. The features and genesis of the dalangtan salt deposit in the qaidam basin. *Bull. Chin. Aca. Geol. Sci.*, 1993, 26: 95-114.

[5] Han J. Preparation of high quality potassium chloride with magnesium sulfate subtype brine from dayantan. *Ind. Miner. Proc.*, 2011, 5 (3): 7-11.

[6] G. P. Tan, L. Ma, X. G. Shang. The deposit character and formation cause of dalangtan liangzhong flat kalium-magnesium deposite. *Eng. Sci.*, 2005, 9 (7): 306-310.

[7] J. L. Pei, Z. M. Sun, X. S. Wang, Y. Zhao. Evidence for tibetan plateau uplift in Qaidam basin before eocene-oligocene boundary and its climatic implications. *J. Earth Sci.*, 2009, 20: 430–437.

[8] Z. Nie, L. Z. Bu, J. H. Liu, Y. S. Wang, M. P. Zhen. Status of potash resources in salt lakes and progress in potash technologies in china. *Acta Geoscientica Sinica*, 2010, 31: 869-874.

[9] G F Ran, H Z Ma, R Y Meng. Rapid determination of potassium content by sodium tetraphenyl boron-quaternary ammonium salt volumetric method. *J. Salt Lakes Res.*, 2009, 17 (2): 39-42.

[10] Y. D. Wang. Preliminary study on the method for dissolution mining of the low grade solid potassium deposit in mahai salt lake. *J. Salt Lake Res.*, 2006, 14 (1): 24-28.

[11] Y. Q. Cai. Exploitation and utilization of salt lake mineral resources in the basin of chaidamu. *China Geo. Min. Eco.*, 2003, 2: 11-14.

[12] C. B. Li, X. C. Zhang. Status quo of development of potassium resource in chaerhan salt lake in qinghai. *Morden Min.*, 2009, 2: 16-19.

[13] H G Cheng, N Wang, X C Pan, J Y Ma, Z H Zhao, F Q Cheng. The effect of sulfate content on the carnallite quality precipitated from brine. *J. Chem. Pharmaceutical Res.*, 2013, 5 (9): 453-458.

[14] Z. M Jin, H. N Zhou, L. S. Wang. Study on metastable phase equilibria of quinary system at 157℃, *Chem. J. Chin. Univer.*, 2002, 23 (4): 690-694.

[15] Z. M Jin, H. N Zhou, L. S. Wang. Study on metastable phase equilibria of quinary system at 35 ℃. *Chem. J. Chin. Univer.*, 2001, 22 (4): 634-638.

[16] Z. M. Jin, X. Z. Xiao, S. M. Liang. Study on metastable phase equilibria of quinary system（Na^+、K^+、Mg^{2+}), (Cl^-、SO_4^{2-}), H_2O. *Acta Chimica Sinica*, 1980, 38 (4): 313-321.

[17] Z. D. Niu, F. Q. Cheng, B.C. Li. Phase diagram and its application of salt water system. *Tianjin University press: Tianjin*, 2002, 2:156-174.

[18] P. S. Song, X. H. Du, H. C. Xu. Phase equilibrium and properties of the saturated solution in the ternary system $Li_2B_4O_7$-Li_2SO_4-H_2O at 25℃, *Chin. Sci. Bull.*, 1983, 2: 106-110.

[19] P. S. Song, H. B. Fu, Solubilities and properties of solution in the reciprocal system Li, Mg^{2+}// SO_4^{2-}, $B_4O_7^{2}$-H_2O at 25℃, *J. Chin. Inorg. Chem.*, 1991, 7: 344-348.

[20] P. S. Song, X. H. Du. Phase equilibrium and properties of the saturated solution in the quarternary system $Li_2B_4O_7$-Li_2SO_4-LiCl-H_2O at 25℃, *Chin. Sci. Bull.*, 1986, 31: 1338-1343.

[21] S. K. Bhattacharia, S. Tanveer. Thermodynamic modeling of aqueous Na^+–K^+–Mg^{2+}–SO_4^{2-} quaternary system. *Fluid Phase Equilibria*, 2015, 404: 141-149.

[22] S. K. Bhattacharia, N. Hossain. Thermodynamic modeling of aqueous Na^+–K^+–Mg^{2+}–SO_4^{2-} quaternary system with electrolyte NRTL model. *Fluid Phase Equilibria*, 2015, 403: 1-9.

[23] M. Steiger, K. Linnow. Decomposition reactions of magnesium sulfate hydrates and phase equilibria in the $MgSO_4$–H_2O and Na^+–Mg^{2+}–Cl^-–SO_4^{2-}–H_2O systems with implications for Mars. *Geochim. Cosmochim. Ac.*, 2011, 75 (12): 3600-3626.

[24] M. S. M. Abdel Wahed, E. A. Mohamed. Crystallization sequence during evaporation of a high concentrated brine involving the system Na^+–K^+–Mg^{2+}–Cl^-–SO^{4-}-H_2O. *Desalination*, 2015, 355: 11-21.