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Research Article

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The effect of sulfate content on the carnallite quality precipitated from brine

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ABSTRACT

The existing large amount of sulfate in brine has a huge effect on carnallite precipitation during the process of producing carnallite from salt field. A series of experiments of effect of different sulfate concentration on carnallite quality precipitated from brine were conducted. The results indicated that sulfate in brine could have a huge effect on carnallite quality at the condition when sulfate content were at a high level or evaporating brine at high temperature. In addition, the content of sulfate in solid products at the carnallite precipitation stage is the highest when sulfate content is 2% in the simulated brine. Results from laboratory experiments show that sulfate has a certain effect on producing carnallite, it have some degree of guiding significance in process optimization of producing carnallite.

Keywords: brine; carnallite; sulfate; evaporation

INTRODUCTION

Solubility potash salt which mainly consist of potassium chloride and potassium sulfate are lacking mineral resources of China as raw material of potassium fertilizer[1,2]. As a vast agricultural country, China is in great demand of potassium fertilizer. Therefore, to meet the demand of agricultural potassium fertilizer, China need to spend large amounts of foreign exchange to import, among which 70% depend on imports[3-5]. In order to increase self supply rate of potassium salt and guarantee agricultural sustainable development, it is of great importance and urgence to realize effective utilization of potassium resources.

Mahai Salt Lake lies to the northwest of Qaidam Basin. It has been known as a potash-magnesium salt deposit, including sylvinite mine and liquid mine[6,7]. Owing to long-term and single development of potassium fertilizer, salt lake brine has been aging and resulted in a waste of resources. On the other hand, the low grade solid mine is increasing year by year. In current industrial practice, dissolving brine has become a major method to make full use of the low grade solid mine[8]. In addition, the dissolved brine also become an important source of preparing carnallite which acts as raw material of producing potassium chloride.

As is known, the process of extracting potassium chloride from brine containing potassium is using carnallite as raw material to prepare and produce potassium chloride[9-11]. Salt field operation of carnallite from brine containing potassium mainly used brine as raw material. Commonly, the solar energy and wind energy were used to evaporate, concentrate, crystallize and then separate common salt. One of the major product is carnallite [12-15]. The dissolved brine of Mahai Salt Lake resulted from long-term non-balance mining, a lot of sulfate enriched. As a result, the production of carnallite contains a certain amount of sulfate impurity, thus leading to a low purity and grade of carnallite [12,15].

To summarize experiments of long-term indoor evaporation and field equipment evaporation, a phenomenon has been found that there existing a great quantity of sulfate in carnallite products. However, sulfate has a great effect on precipitation of carnallite to some degrees. Hereby, in order to determine the relationship between sulfate content in brine with quality of products precipitating in brine containing different sulfate content and evaporating at different temperature, investigation of effect of sulfate content on carnallite was examined.

Experimental Procedures

(1)The experiments were performed in Qaidam Basin in Qinghai Province, China[16]. The various composition of thepreparation of brine was shown at Table1. The addition of SO_4^{2-} respectively were 1%, 2%, 3%, 5% and 10%, according to the weight percentage of brine. In order to guarantee the stable system point on phase diagram, the additional SO_4^{2-} were tansformed into Na_2SO_4, K_2SO_4, $MgSO_4$ under the rules of equal weight. It was present at Table2.

Table.1 Chemical Composition of Brine

Irons	K^+	Na^+	Mg^{2+}	Cl^-	H_2O
Content[wt%]	0.62	7.73	1.39	15.83	72.67

Table.2 Chemical Composition of Brine Containing Different Sulfate Content

Chemical ontent[wt%]	Sulfate Content[%]				
	1	2	3	5	10
KCl	1.28	1.12	1.1	0.98	0.68
NaCl	18.39	16.08	15.8	14.08	9.76
$MgCl_2$	4.35	5.34	4.59	4.09	2.84
K_2SO_4	-	0.19	0.21	0.35	0.7
Na_2SO_4	-	2.81	3.14	5.24	10.47
$MgSO_4$	1.25	-	0.95	1.58	3.17
H_2O	74.73	74.47	74.21	73.68	72.38

(2)The brine respectively containing 2% and 5% SO_4^{2-} were took as examples. Firstly, adding NaCl which takes 5% of brine weight(That is 50g of NaCl) to change the ratio of Na/(K-Mg) of the system. Secondly, adding KCl which takes 5% of brine weight(That is 50g of KaCl) to change the ratio of K/(Na-Mg) of the system. Finally, adding $MgCl_2$ which takes 5% of brine weight(That is 50g of $MgCl_2$) to change the ratio of Mg/(K-Na) of the system.

(3)The brine mentioned above were evaporate at 75℃, there were solid precipitated from brine continually during the process of evaporation. The sample of solid were classified into several groups and then the content of K^+, Na^+, Mg^{2+}, Cl^- and SO_4^{2-} were analysed.

RESULTS AND DISCUSSION

3.1The sulfate content in solid phase of brine containing different content of sulfate during evaporation

The brine respectively containing 1%, 2%, 3%, 5% and 10% SO_4^{2-} were evaporated. During the evaporation, it was found out that there were still no solid precipitation until evaporated water exceeded 40%. Therefore,the SO_4^{2-} content in solid phase precipitated from brine respectively containing 1%, 2%, 3% and 5% SO_4^{2-} were compared, which was shown at Fig.1.

At the evaporation of prophase(when evaporation rate is low), the SO_4^{2-} content in solid phase is proportional to sulfate content in brine.In other words, when SO_4^{2-} content in brine is at a low level, the SO_4^{2-} content in solid phase is low. With the evaporation reaching the later period(when evaporation is 0.5155), the SO_4^{2-} content in solid phase of brine containing 2% and 5% SO_4^{2-} increasing rapidly. In addition,there is a positive correlation between SO_4^{2-} content in both solid phase and in brine.

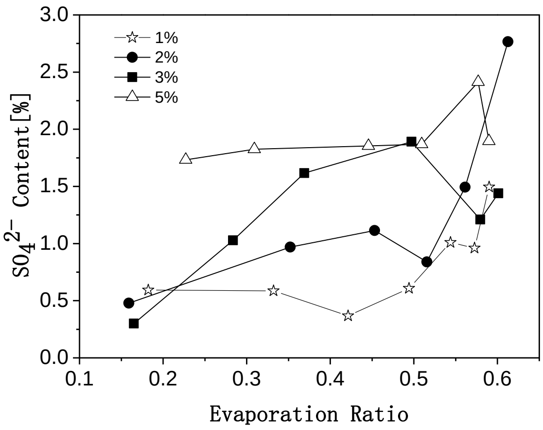

Fig.1 Changes of SO_4^{2-} Content in Solid Phase

3.2 Evaporation Experiments of Different Proportion of K\Na\Mg

(1)When the brine contains 2% sulfate, 5%KCl, 5%NaCl and 5%$MgCl_2$ were added. The results of changes of K^+, SO_4^{2-} with the changing of evaporation rate were shown at Fig.2, Fig.3 and Fig.4.

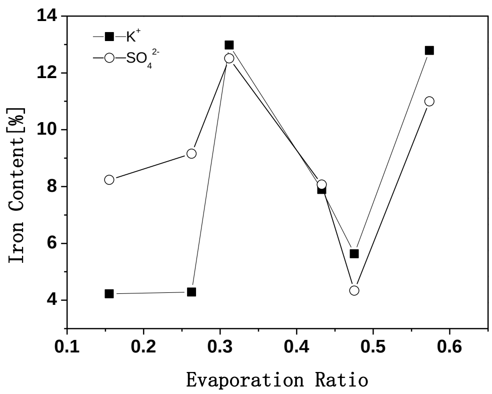

Fig.2 Changes of K^+ and SO_4^{2-} Content in Solid Phase with the addition of KCl

It can be seen from Fig.2 that the addition of KCl results in substantially increasing of K^+, at the same time, the proportion relation between K^+ and other irons also changes. With the evaporation of brine, the changes of K^+ and SO_4^{2-} content in solid phase are almost consistent. By the way, K^+ content in solid phase is at a high level. When evaporation rate is 0.312, K^+ content reaches its maximum value of 12.98%.

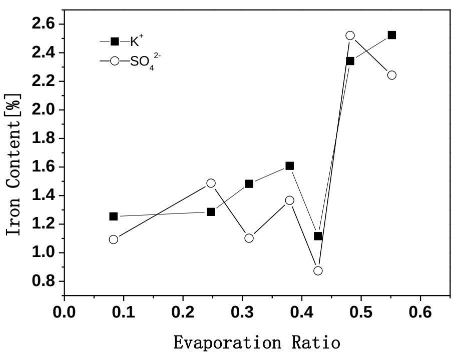

Fig.3 Changes of K^+ and SO_4^{2-} Content in Solid Phase with the addition of NaCl

The addition of 5% NaCL leads to the proportion relation between K^+ and other irons changing. According to the theory of quaternary system phase diagram of Na^+, K^+, Mg^{2+}//Cl^--H_2O [17-20], the addition of NaCl could not change the crystallization path of evaporation of brine, it could only lead to the lag of carnallite precipitation.It can be seen from Fig.3, evaporation of 0.428 is the turning point both of K^+ and SO_4^{2-} precipitation. But when evaporation rate is more than 0.482, the K^+ content is increasing with the evaporation rate increasing until the end of evaporation whereas the

SO_4^{2-}content tends to decrease. A conclusion can be drawn that the precipitation of K^+ and SO_4^{2-} are asynchrony, and K^+ is mostly precipitated in the form of KCl.

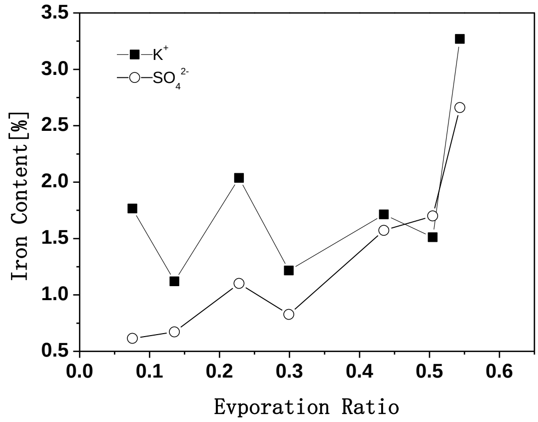

Fig.4 Changes of K^+ and SO_4^{2-} Content in Solid Phase with the addition of $MgCl_2$

In the same condition,adding extra 5% $MgCl_2$ to change the K^+/Mg^{2+} value. Fig.4, Fig.5 and Fig.6 are compared, it can be seen that with the addition of $MgCl_2$,SO_4^{2-} content observably decreases.When adding 5%KCl into brine,SO_4^{2-} content in solid phase reaches as far as 2.5% in the initial stage;when adding 5%NaCl into brine, SO_4^{2-} content in solid phase also reaches 1.5%; when adding 5% $MgCl_2$, SO_4^{2-} content in solid phase is only 0.65% in the initial stage. The results show that the addition of $MgCl_2$ inhibit the precipitation of SO_4^{2-}.

(2)When the brine contains 5% sulfate, 5%KCl, 5%NaCl and 5%$MgCl_2$ were added. The results of changes of K^+, SO_4^{2-} with the changing of evaporation rate were shown at Fig.5, Fig.6 and Fig.7.

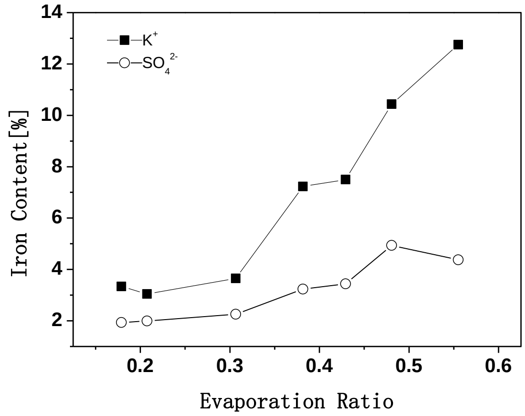

Fig.5 Changes of K^+ and SO_4^{2-} Content in Solid Phase with the addition of KCl

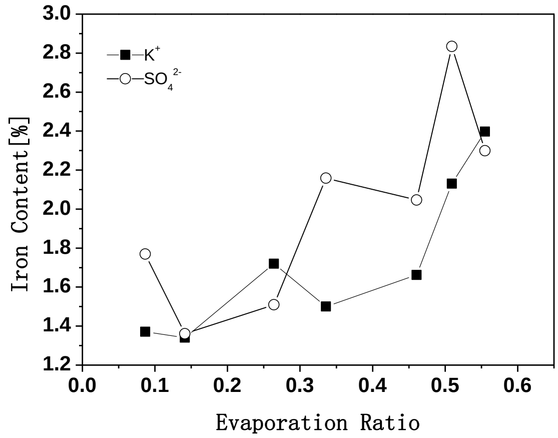

Fig.6 Changes of K^+ and SO_4^{2-} Content in Solid Phase with the addition of NaCl

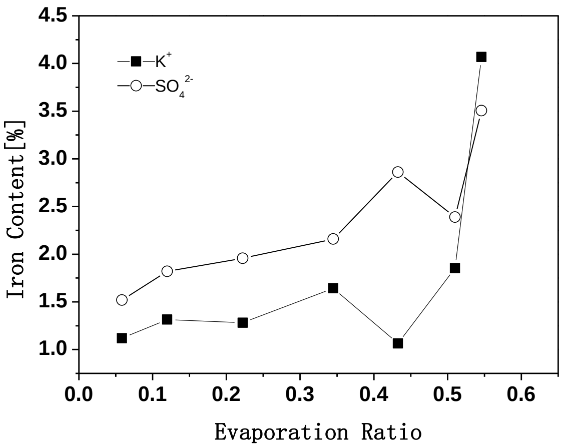

Fig.7 Changes of K^+ and SO_4^{2-} Content in Solid Phase with the addition of $MgCl_2$

It can be seen that K^+ content is gradually increasing with the evaporation increasing when compared Fig.5 with Fig.2; the K^+ content in Fig.5 has no significance law; in Fig.7, the K^+ precipitation content stays low in the initial stage,when evaporation rate is more than 0.43, the K^+ precipitation content increases significantly.

Summary

When SO_4^{2-} content in brine is at a low level, room temperature evaporation condition could not change the crystallization path of evaporation of chloride brine. But in the situation when SO_4^{2-} content is high or evaporating at high temperature, the SO_4^{2-} content in brine has a huge effect on carnallite quality precipitated from brine.

When SO_4^{2-} content in brine is 2%, the SO_4^{2-} content in brine during the carnallite precipitation stage is highest among all the brine.
When SO_4^{2-} content in brine is more than 5%, the solubility of brine increases. There is still no solid precipitated from brine until a large quality of water has been evaporated. In addition,the SO_4^{2-} content in solid phase has no no significance law during the evaporation.

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