



Model for the decomposition of carnallite in aqueous solution



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ARTICLE INFO

Article history:

Received 13 November 2013

Received in revised form 16 September 2014

Accepted 21 April 2015

Available online 23 April 2015

Keywords:

Carnallite

Decomposition ratio

Temperature

Water amount

ABSTRACT

Carnallite is a double salt ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), which is a common source of potassium chloride (KCl). It is treated with a mother liquor containing magnesium chloride (MgCl_2), KCl and sodium chloride (NaCl), and then KCl and NaCl precipitate in the mother liquor solution. The amount of water and the temperature are the two crucial factors for the decomposition of carnallite in aqueous solution. Because of the lack of research on the decomposition process of carnallite, the yield and quality of the KCl produced are limited. In this study, we develop a model for the decomposition of carnallite based on the multi-temperature quaternary diagram of the $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ system and the principle of mass conservation for MgCl_2 . The model is verified using experimental and literature data for different types of carnallite: normal, Mg-rich, Na-rich, and (Mg and Na)-rich. The proposed model predicts the amount of water required for decomposition of carnallite and the yield of KCl very well for normal and Mg-rich carnallite (within 2%), for Na-rich and (Mg and Na)-rich carnallite (within 8%), and for ancient evaporite carnallite in Laos (within 2%).

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1. Introduction

Potassium chloride is an important chemical fertilizer in agriculture (Harper et al., 2012; Chen et al., 2013; Cheng et al., 2013). A source of KCl is the carnallite double salt, which has the composition $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, and is either obtained as the ore or recovered from brine that favors carnallite formation (Dave and Ghosh, 2006). Irrespective of its origin, carnallite is treated with decomposition mother liquor containing MgCl_2 , KCl, and NaCl, so that KCl and NaCl are precipitated in the equilibrium mother liquor. The driving force for decomposition is the difference in the concentration at the experimental temperature and the saturation of equilibrium mother liquor (Mohameed et al., 2002). The key factor is the amount of water used to dissolve MgCl_2 . This water causes the carnallite to decompose to its components. As is shown in Fig. 1(A), if the MgCl_2 concentration is at or near the triple-saturation point (the point at which the solution is saturated with carnallite, NaCl, and KCl), the solubility of KCl is suppressed to the point where most of the KCl will precipitate (Liu et al., 2007). Moreover, the composition of the triple-saturation point changes with temperature (Fig. 1(B)). For maximum recovery of the components, the crystallizing mixture must be saturated with carnallite at its triple-saturation point. If the mixture is not saturated, then KCl will dissolve in the water. If the amount of water is not suitable or inadequate, carnallite will not decompose in the aqueous solution. Generally, the amount of water used to dissolve carnallite and the reaction

temperature are two important factors that restrict KCl production. In the crystallization processes, the solid–liquid phase equilibrium is very important. Furthermore, owing to the lack of a systematic study about the decomposition process of carnallite in aqueous solution by the solid–liquid phase equilibrium method, the yield and quality of KCl produced are limited. Here, a functional model for the amount of water and the decomposition ratio of carnallite in aqueous solution is established and evaluated from 256.15 to 323.15 K in quaternary solid–liquid phase equilibrium systems based on the mass transfer equilibrium of MgCl_2 between the precipitated salts and the ionic species remaining in solution (Ettouney, 2006; Demming et al., 2008; Ji et al., 2010).

As discussed above, we found that the water amount and decomposition ratio of carnallite are related to the temperature and composition of the equilibrium mother liquor. The model for the effect of the system properties on the decomposition process of carnallite was established by the multi-temperature quaternary diagram data of the $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ system. This model and the decomposition process of modern solar-pond carnallite in the Qarhan Salt Lakes and ancient evaporite carnallite in Laos are discussed.

2. Experimental

2.1. Materials

Carnallite was taken from the drilling core of Vientiane potash deposits in Laos. Its composition (Table 1) indicates that the carnallite is pure. The content of water-insoluble material in the carnallite was less than 0.5%. Doubly-distilled water was used in all the experiments, as well as for the analytical measurements. Standard glassware was

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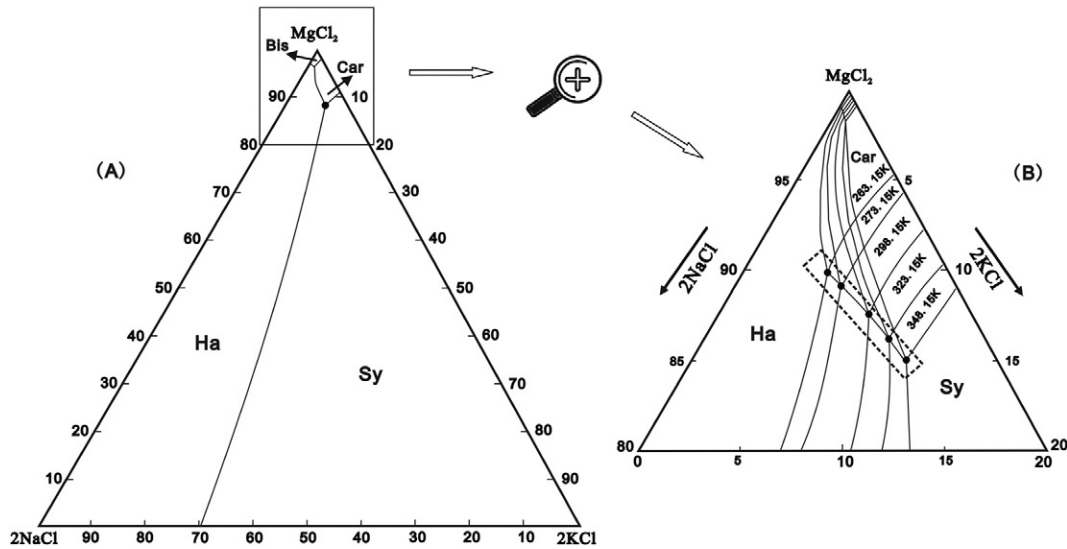


Fig. 1. Quaternary diagram of NaCl–KCl–MgCl₂–H₂O system. (A) at 298.15 K. (B) Partially enlarged multi-temperature from 263.15 to 348.15 K. (•) triple-saturation point, (Sy) KCl, (Ha) NaCl, (Car) KCl·MgCl₂·6H₂O, and (Bis) MgCl₂·6H₂O.

used in all experiments. Whenever heating was required, a super constant temperature water-bath (HH-501, Shanghai Qiqian Electronic Technology Co. Ltd., China) was used. The solid phases were obtained by vacuum filter (SHZ-3 circulating water vacuum pump, Shanghai Yarong Biochemistry Factory, China) separation.

2.2. Analytical methods

The ionic compositions of the liquid and solid phases were determined using well-established procedures. The Mg²⁺ ion concentration was determined by complexometric titration with EDTA standard solution with an accuracy of ±0.5%. The K⁺ ion concentration was determined by gravimetric method with sodium tetraphenylborate with an accuracy of ±0.3%. The Cl⁻ ion concentration was determined by Hg(NO₃)₂ titration with an accuracy of ±0.5%. The Na⁺ ion concentration was calculated by the ion-equilibrium subtraction method with an accuracy of ±1%.

2.3. Experimental procedures

The decomposition process of carnallite in aqueous solution is an endothermic reaction, and was carried out in a super constant temperature water-bath. The reaction temperature was controlled at 293.15 K (ambient temperature). The speed of the agitator was 600 rpm. The reaction time was 45 min, and 2000 ml standard glassware was used as the reaction vessel. The solid-phase minerals and liquid-phase solution were separated by vacuum filtration after the end of decomposition.

Because there is water adsorbed to the crystals/minerals in the products of the decomposition, it is necessary to remove this water and discuss the experimental results in this study. There are four methods for the removal of this solution: (1) Washing with an organic solvent (Moretto, 1988; García-Veigas et al., 2009) (e.g. ethanol,

ethanol–glycol, or acetone), yet the effect of salting-out in organic solvent with high salinity would occur (Xu et al., 1991). (2) Washing with doubly-distilled water (McCaffrey et al., 1987), but some of crystals/minerals would dissolve because mineral salts are soluble. (3) Obtaining large-grained crystals with 5 mm in diameter by crystallization, and then the water adsorbed to the crystal surfaces can be removed by tissues (Siemann and Schramm, 2000). However, the KCl particle size at the end of decomposition is generally very small (<0.5 mm) (Mohameed et al., 2002; Li et al., 2009) and it is difficult to avoid fluid inclusion. (4) Removal with the evaporation of mother liquor method (Herrmann, 1980). This method has been applied to research the crystallization behavior of borate during the brine evaporation process (Gao and Li, 1982). The pure solid phase of precipitation is obtained through deducting the solution attached to the crystal/mineral surfaces. The ionic composition of the equilibrium mother liquid is constant at the desired temperature, and was accurately determined. Furthermore, the amount of water in the equilibrium mother liquid is known. To estimate fluid inclusion, method (4) was applied. The product crystals/minerals obtained from decomposition were placed in a drying oven on forced convection at 373.15 K for 4 h (Cheng et al., 2009). The amount of water adsorbed to the crystal/mineral surface was calculated based on the loss of weight with the drying method.

Additionally, the mass of the product is always lower than the mass of the feed because of the viscosity of the brine and solution adsorbing to the surface of the container during the experiments. When the quantity of the solid phase in the product is weighed by electronic balance with an accuracy of ±0.01 g, the loss of mass of the system is the quantity of the liquid phase, which can be calculated by the mass balance of the feed and the product. The components of the liquid phase are constant at the desired temperature. Therefore, we can estimate the decomposition ratio of carnallite based on our experimental results.

The decomposition ratio of carnallite in aqueous solution includes the KCl yield and the MgCl₂ decomposition yield. The KCl yield is given by

$$\varepsilon_{KCl} = \frac{M_{KCl(S)} - M_{KCl(L)}}{M_{KCl(S)}} \cdot 100\% \tag{1}$$

The MgCl₂ decomposition yield is given by

$$\varepsilon_{MgCl_2} = \frac{M_{MgCl_2(L)}}{M_{MgCl_2(S)}} \cdot 100\% \tag{2}$$

Table 1
The composition of carnallite from the drilling core of Vientiane potash deposits in Laos.

Ion concentration, wt.%				Substance components, wt.%				
K	Mg	Cl	Na	KCl	NaCl	MgCl ₂	H ₂ O	Water-insoluble material
8.34	5.35	46.84	15.35	15.90	39.02	20.96	23.76	0.36

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