

Crystallization Process Investigation of Potassium

Chloride from Carnallite Decomposition

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The crystallization process for producing potassium chloride from carnallite was studied in a continuous operated system. The crystallization mechanism was experimentally studied for making KCl crystal from solid carnallite, and the factors affecting the crystal size and size distribution were investigated. The effects of residence time and $MgCl_2$ concentration in mother liquor on crystallization process and product crystal size were also studied. Furthermore, the crystallization kinetics of potassium chloride was reported for the system.

1. Introduction

The technology for production of potassium chloride depends on the resources of raw material, such as the solution from seawater or salt lake. If the raw material is relatively pure solution of KCl, cooling crystallization is commonly employed. However, if the production is based on the solution of salt lake or the brine from seawater, the potassium chloride is normally produced from a solid form of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) (Yang Hongmei, 2003). The basic thermodynamic theory of separating KCl from carnallite is shown in Fig.1, which is a phase diagram of KCl- $MgCl_2$ - H_2O system at 20 °C. If water is added with exactly required amount into pure carnallite (point G, solid), the system point in the diagram will move from G to point D. During the process of water addition, carnallite will be decomposed and the system will become a solid phase of KCl (point A) and solution (point P).

The production of potassium chloride from carnallite includes many basic processes so that the size of product is difficult to control. On the other hand, the reported data on crystallization kinetics for potassium chloride were based on pure potassium chloride

solution (Hong Xianlan et al., 1994 and Xia Shuping et al., 1993). Crystallization kinetics is the vital factors affecting in the crystallization process (Randolph Alan D et al., 1988 and Mydlaz J. et al., 1993). But the kinetic data obtained from pure solution can't be directly used for the crystallization process from solid carnallite. Moreover, the crystallization process of potassium chloride from carnallite is more complicated because the KCl crystals formed from a solid phase of carnallite. Therefore, the crystallization mechanism is very important for the process controlling.

The aim of this work is to clarify the basic crystallization mechanism of potassium chloride from carnallite. Furthermore, the crystallization kinetics and the effect of operation conditions on particle size distribution were studied. The method for controlling the particle size distribution was also proposed.

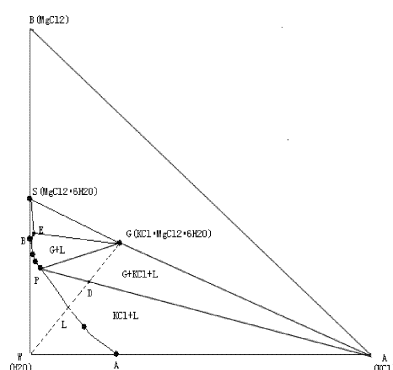


Figure 1: Phase diagram of $KCl-MgCl_2-H_2O$ system at 20

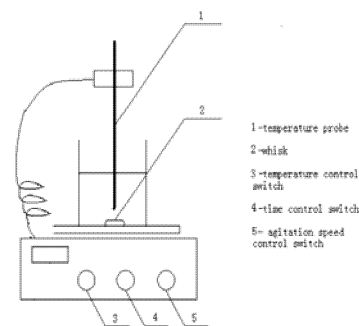


Figure 2: Experimental set-up

2 . The mechanism of KCl crystallization from carnallite decomposition

2.1 Experiments set up

The KCl crystal forming can be thought as two mechanisms. The one was saying as that the KCl in carnallite crystals shrinks into pure KCl crystals. It means that the KCl in a solid carnallite crystals directly become another solid phase. Another one is that KCl is first transferred to liquid phase from solid carnallite phase, and then was crystallized from solution. In order to clarify the mechanisms of KCl crystal forming from carnallite, the experimental was arranged as follows. The raw material of carnallite used in the experiments was provided by Qinghai Saline Lake Industrial Groups. 300 ml of water was firstly added into a vessel, and temperature was controlled at a constant 20 during the whole process. Then, a weighted amount of solid carnallite was added into the water

and mixed for 30 minutes. The clear solution was sampled for determining the concentration of K^+ , Mg^{2+} and Cl^- by titration. The experiments were repeated with different amounts of carnallite. The system used in the experiments is given in Fig.2.

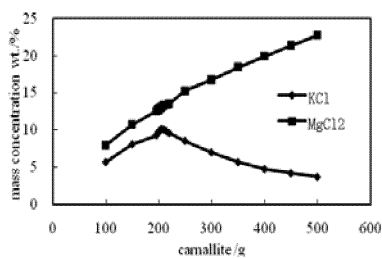


Figure 3: the concentration of KCl, $MgCl_2$ in the solution at different amounts of carnallite added

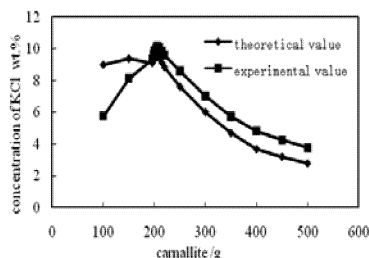


Figure 4: Comparison of KCl concentration obtained from experiment with saturated solution

2.2 Results and discussion

The measured concentration of KCl, $MgCl_2$ in liquid phase for different added amounts of carnallite are given in Fig.3. From Fig.3 it can be seen that the concentration of $MgCl_2$ is continuously increased with an increase of the added amount of carnallite. However, the concentration of KCl was firstly increased with the increase of added carnallite and then decreased. It means that KCl was first dissolved into liquid phase, and then crystallized from solution when enough amount of carnallite was added.

The measured KCl concentration during the carnallite adding was compared with the saturated concentration of KCl in the solution with the same amount of $MgCl_2$ as shown in Fig.4. From Fig.4 it can be clearly seen that the measured concentration of KCl was higher than that in the saturated solution. It means that the supersaturation of KCl was existing during crystallization process. Therefore, it can be concluded that the production process of KCl from carnallite solid undergoes two steps. Firstly, carnallite was decomposed by water, and then KCl was crystallized from the solution. Therefore, the crystallization process can be affected by the two steps. The factors which affect the decomposition rate of carnallite include the $MgCl_2$ concentration in the solution, temperature and mixing intensity. If the decomposition rate of carnallite is reduced the supersaturation of KCl will be decreased under the same crystallization conditions. Therefore, the concentration of $MgCl_2$ in mother liquor might be an important factor for the KCl crystallization process. On the other hand, the supersaturation of KCl depends on the growth rate and the amount of KCl crystal in the system. Therefore, it is

necessary to investigate the effect of MgCl_2 concentration on the crystallization process of KCl and its crystallization kinetics.

3. Crystallization kinetics

3.1 Experiments set up

A continuous operated system was employed for this study. The experiments were carried out in a Draft Tube Baffle (DTB) crystallizer. The volume of crystallizer is 20 L, and mixing was provided by a four 45° pitch blade propeller. Samples were taken after the system was operated longer than 8 times residence time. The size distribution of product crystals was analyzed by LS-13320 laser diffraction particle size analyzer (American Beckmann the Coulter co., ltd). As analyzed above, the decomposition rate of carnallite depends on the concentration of MgCl_2 in the mother liquor, which is the very important factor to affect the creation rate of KCl supersaturation. The de-supersaturation rate of KCl is dependent on kinetics in the system. Therefore, the concentration of MgCl_2 in the mother liquor and the feed rate of carnallite, which was used for the calculation of residence time, were altered as process variables for determining the crystallization kinetics. The concentration of MgCl_2 in the decomposition liquor was adjusted by the ratio of mother liquor and added fresh water. The amount of added water was calculated based on the feed rate of carnallite in order to make the carnallite fully decomposition.

3.2 Results and discussion

The crystallization kinetic data were estimated based on Mixed Suspension, Mixed Particle Removal (MSMPR) model. The particle size distributions in the product line at different process times and at different locations in the crystallizer were tested. It was satisfied for the requirement of the MSMPR model.

All the experimental data was treated with MSMPR model. The obtained nucleation rate was correlated as

$$B = 6.65 \times 10^8 \times (\Delta C)^{1.464} \quad (1)$$

The growth rate was correlated as

$$G = 10^{1.5316} \times (\Delta C)^{0.4746} \quad (2)$$

Where B is the nucleation rate of crystals ($\mu\text{m/h}$), G was growth rate of crystals ($\mu\text{m/h}$), and ΔC is the supersaturation (g/L).

4. Factors influencing product crystal size

The experimental set up is the same as used for kinetic study for the study in this section.

4.1 The influence of $MgCl_2$ concentration on product size distribution

The particle size distributions obtained from various concentrations of $MgCl_2$ in the mother liquor are shown in Fig. 5. When the residence time is fixed, the product size of KCl increases with the increase of $MgCl_2$ concentration in the mother liquor. A large particle size can be obtained at higher $MgCl_2$ concentration in the mother liquor. This is because higher concentration of $MgCl_2$ in the mother liquor can reduce the decomposition rate of carnallite. The creation rate of KCl supersaturation can be decreased. The level of supersaturation could become lower. Therefore, crystals with larger size were produced. From this result it can be concluded that the concentration of $MgCl_2$ in mother liquor is an important parameter for controlling the product size in this crystallization process.

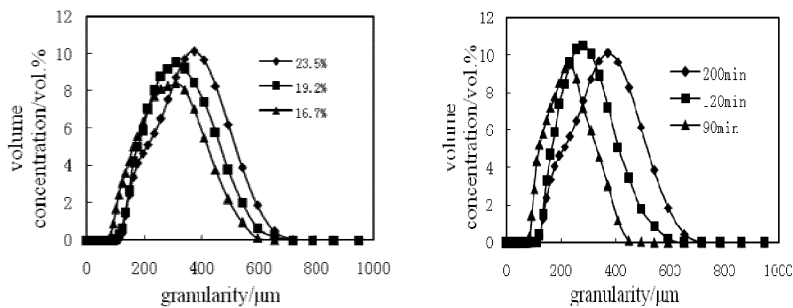


Figure 5: KCl grain-size distributions when the residence time is 120 min
Figure 6: KCl crystal size distributions when the $MgCl_2$ density is 23%

4.2 The influence of residence time

The residence time was defined as the time from particle enters the crystallizer to leave it when the system was steady. Experimental particle size distributions at different residence times are given in Fig.6 for case of the $MgCl_2$ concentration in the mother liquor is 20 wt%. Under fixed $MgCl_2$ concentration in the mother liquor, the KCl product size increases with the increase of residence time. This is because the supersaturation level is lower at long residence time than that at short residence time. These results show that crystals of large particle size can be produced by using relatively long residence time.

5. Conclusions

The crystallization mechanism was experimentally investigated for the crystallization process of KCl from carnallite decomposition method. It was found that the crystallization process of KCl has two steps. KCl was first transferred from carnallite solid into the solution, and then was crystallized from supersaturated solution. The crystallization of KCl from carnallite decomposition process was investigated based on the crystallization mechanism. The results showed that residence time and $MgCl_2$ concentration in composition solution are important factors affecting the product crystal size.

Acknowledgments

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