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Crystallization Process of Calcium Sulfate Dihydrate in Gypsum Type Brine System

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1 Introduction

Calcium sulfate deposition is one of the most important and serious problems faced by heat transfer equipment during operation (Pavlos et al., 1999; Liu et al., 1996).The crystallization of calcium sulfate is known as a major engineering problem in process industries, since deposits on heat transfer surfaces create a barrier to the transmission of heat, increasing pressure drop and promoting corrosion of tube material (David et al., 2001; Alimi et al., 2003; David, 1981). Unfortunately, the crystallization process of calcium sulfate dihydrate in plaster brine system had not been reported as far as we know.

Brine, containing high concentrations of calcium sulfate dihydrate, was discharged in the process of producing vacuum salt from Haolong Salt Chemical Co., Ltds. Then, the calcium sulfate dihydrate was recovered as by-product from brine after draining off in subsides, and the clear overflowing liquid was reused. The study on the suitable additives and optimum condition of the calcium sulfate dihydrate crystallization was helpful for obtaining more calcium sulfate dihydrate as well as reducing the negative impact of pipeline. Meanwhile, calcium sulfate dihydrate was widely applied in industry (Taha et al., 1995). As a result, the study on calcium sulfate dihydrate crystallization will generate potential economic benefits by production of calcium sulfate dihydrate and protection against pipeline corrosion.

In this work, different conditions in the atmospheric evaporation crystallization process were studied to determine optimum condition. The effect of stirring rate, retention time, weight of seed and evaporation temperature on average size of $CaSO_4•2H_2O$ in the crystallization process was investigated. Then, the optimum conditions of the calcium sulfate dihydrate crystallization in gypsum type brine system were determined.

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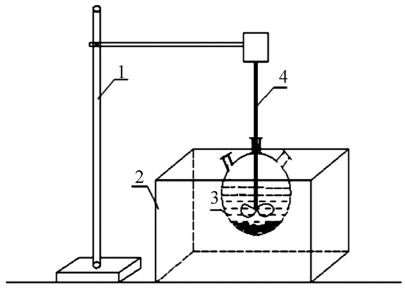

Fig.1. Device for the crystallization of calcium sulfate dihydrate in plaster brine system.

2 Apparatus and Procedure

The experiment device was shown in Figure 1. A certain volume of feed solution and calcium sulfate dihydrate were added into a three-neck flask under experimental temperature to prepare a plaster saturated solution. The plaster saturated solution was isothermally evaporated at specified stirring rate by tuning seed weight and retention time. The particle size distribution of calcium sulfate dihydrate was evaluated using a laser particle size analyzer, from which the effects of different conditions on the average size of calcium sulfate dihydrate were studied.

3 Results and Discussion

The stirring rate played an important role in the crystallization of seed. The precipitation of crystals was not able to suspend uniformly in the mother liquor if the stirring rate was too low, which caused non-uniform mixing, slowing heat and mass transfer . However, the crystal fluid shear stress was increased if the stirring rate was too high, which reduced the crystal size by increasing the secondary nucleation rate and the fragmentation probability in secondary process. The crystal size distribution of calcium sulfate dihydrate at different stirring rate was shown in Fig.2. As shown in Fig.2, the proportion of larger crystals is relatively higher when the stirring rate was 150r/min、250r/min、450r/min、550r/

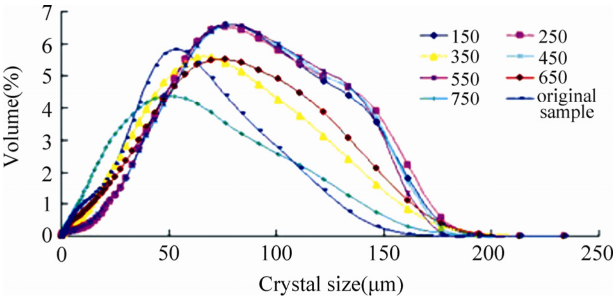

Fig.2. Effect of stirring rate on the crystal size distribution of calcium sulfate dihydrate

min. As a result, the stirring rate was 250r/min in the following experiments unless other noted.

Retention time was an important parameter in the crystallization process. In salt crystallization process, crystal particle size and crystal size distribution was related with crystal nucleation, growth rate and retention time in the crystallizer directly. The thick and uniform crystals were prepared in medium retention time, while, the crystal miniaturization would cause by extreme long or short retention time. In detail, extreme short retention time could result in high crystal population density and tiny crystal for short growth time, however, tiny crystals were already formed and presented in solution because secondary nucleation could occur in extreme long retention time.

Retention time was investigated to observe the effect on crystal size of $CaSO_4•2H_2O$ (stirring rate 250r/min and 4g crystal seed at 60°C). The relationship between the retention time and the crystal size distribution of $CaSO_4•2H_2O$ was shown in Fig.3. The proportion of larger crystals was relatively higher when the retention time was 120min. Therefore, the retention time was determined as 120min in the following experiments unless other noted.

The effect of temperature on the crystallization process of calcium sulfate dihydrate was studied when stirring rate was 250r/min, the retention time was 120min and the weight of crystal seed was 4g. The proportion of larger crystals was relatively higher when the temperature was

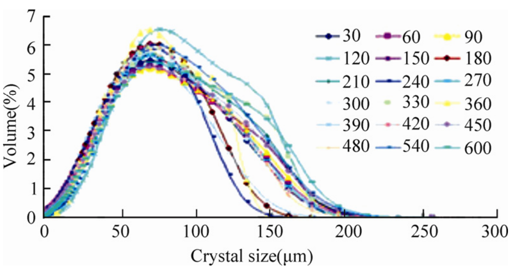

Fig.3. Effect of retention time on the crystal size distribution of calcium sulfate dihydrate

60℃

The weight of crystal seed depended on the weight of solute crystallized, the size of seed and the size of expected products. The effect of weight of seed on the process of calcium sulfate dihydrate was studied under the condition of stirring rate 250r/min and the size of crystal seed 48 ~ 125μm at 60℃. Fig.8 showed the effect of weight of seed on the crystal size distribution.

4 Conclusions

In this work, the key factors in crystallization process of calcium sulfate dihydrate in gypsum type brine system were studied. The crystal product size increased with the increasing of stirring rate at the beginning and the average size of $CaSO_4•2H_2O$ reached 77.24μm when the stirring rate was 250r/min. the average size of $CaSO_4•2H_2O$ increased with the retention time and temperature increasing and it reached 70.39μm when the retention time was 120min and the temperature reached 60 °C respectively, after that it decreased with the increasing of retention time and temperature. Then, orthogonal experimental design was adopted to obtain the optimum technology the crystallization process of calcium sulfate dihydrate, the optimum experimental conditions were: the temperature was 70°C, the stirring rate was 250r/min, the retention time was 120min and the weight of crystal seed was 3g. The line growth rate of calcium sulfate dihydrate was 2.580×10^{-9}m/s in this condition.

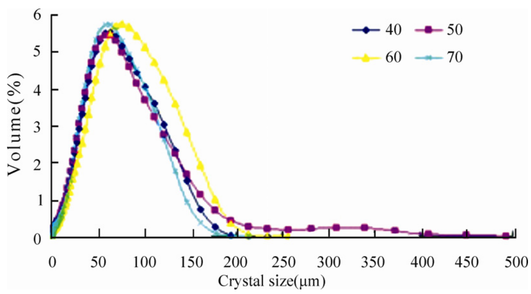

Fig.4. Effect of temperature on the crystal size distribution of calcium sulfate dihydrate

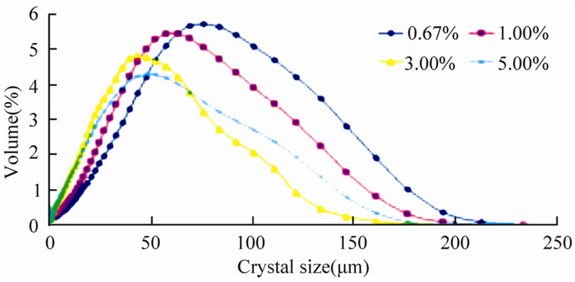

Fig.8. Effect of weight of crystal seed on the crystal size distribution of calcium sulfate dihydrate

Key words: gypsum type brine; calcium sulfate dihydrate; crystallization;crystal growth.

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