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The Effect of Additives on Calcium Sulfate Dihydrate Crystallization Kinetics in Gypsum Type Brine System

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1 Introduction

There exist calcium and sulfate ions outside sodium chloride in solution mining for calcium sulfate brine. The calcium and sulfate ions not only affect the purity of the vacuum salt products, but also increase the scaling of vacuum evaporation tanks and brine reusing pipes. Additives have certain impacts on the crystallization dynamics (Randolph et al., 1971). The crystallization dynamics of calcium sulfate solution system had been studied (Freyer et al., 2003). It was shown that crystallization dynamics and crystal habit were changed with the addition of additives. Herein, the calcium sulfate solubility curve was determined in calcium sulfate type brine. The influence of additives on $CaSO_4$•$2H_2O$ crystallization dynamics in the calcium sulfate brine system with sodium dodecylbenzene sulfonate(SDBS), potassium dichromate($K_2Cr_2O_7$) and polyethylene glycol (PEG) as additives.

2 Experiment

The experimental apparatus was shown in Fig. 1. The constant temperature evaporation experiment was carried out under certain temperature. A certain amount of $CaSO_4 \cdot 2H_2O$ as crystal seed was added into plaster mold brine system. After a moment of crystal growth, the samples were analyzed through laser particle size analyzer. The results showed the influence of crystallization conditions on $CaSO_4 \cdot 2H_2O$ crystallization dynamics.

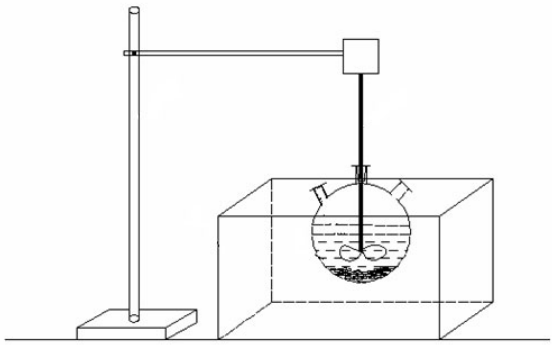

Fig. 1. $CaSO_4$ • $2H_2O$ crystallization apparatus.

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3 Results and Discussions

The $CaSO_4 \cdot 2H_2O$ solubility of gypsum brine type system didn't change significantly with temperature as shown in Fig. 2. At 60°C, the solubility of $CaSO_4 \cdot 2H_2O$ reached its highest level (4.98g/L).

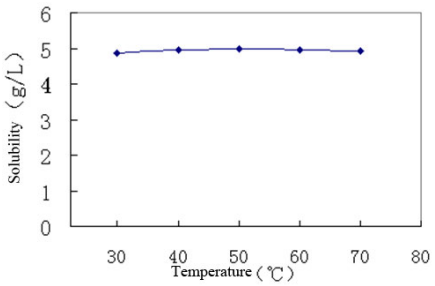

Fig. 2. $CaSO_4$•$2H_2O$ solubility curve of gypsum type brine system.

The experiment condition as follows, stirring speed was 250r/min, standing time was 120min, temperature was 60°C, grain-size of crystal seed was 48～125um, the amount of crystal seed was 4g. The experiment discussed the influence of the additive amount of SDBS on the $CaSO_4 \cdot 2H_2O$ crystallization process. The crystal particle distribution and liner crystal growth rate was affected by the addition of SDBS. When the additive amount of SDBS was 30ppm and 60ppm, the higher proportion of larger particle size had been obtained in Fig. 3,.The liner crystal growth rate was relative larger with addition of 30ppm and 60ppm SDBS as shown in Fig. 4. Considering the cost in industrial application, 30ppm should be chosen as additive concentration.

The experiment condition as follows, stirring speed was 250r/min, standing time was 120min, temperature was

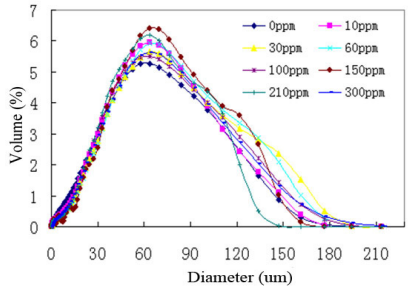

Fig.3 $CaSO_4$•$2H_2O$ crystal diameter distribution with the addition of SDBS

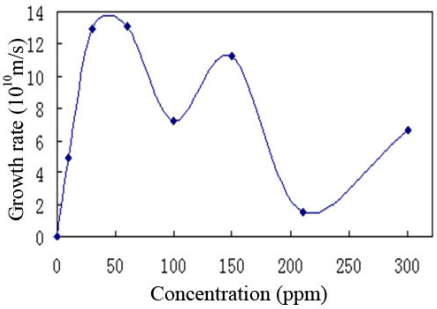

Fig.4 $CaSO_4$•$2H_2O$ crystal growth rate diameter distribution with the addition of SDBS

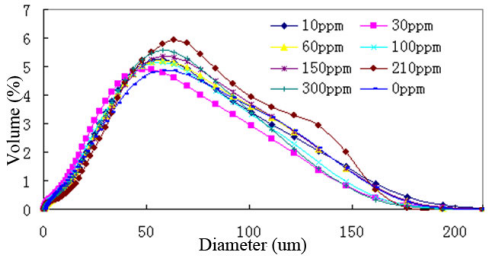

Fig. 5. $CaSO_4$•$2H_2O$ crystal diameter distribution with the addition of $K_2Cr_2O_7$.

60°C, grain-size of crystal seed was 48～125um, the amount of crystal seed was 4g. The experiment discussed the influence of the additive amount of $K_2Cr_2O_7$ on the $CaSO_4$·$2H_2O$ crystallization process.When $K_2Cr_2O_7$ concentration was 210ppm, it is the optimum condition for $CaSO_4$·$2H_2O$ crystallization, which obtain the largest size diameter and linear growth rate as shown in Fig. 5 and Fig. 6. The $CaSO_4$·$2H_2O$ crystallization process was suppressed by too low or too high additive amount of $K_2Cr_2O_7$.

The experiment discussed the influence of the additive amount of PEG on the $CaSO_4$·$2H_2O$ crystallization process. The experiment condition as follows, stirring speed was 250r/min, standing time was 120min, temperature was 60°C, grain-size of crystal seed was 48-125μm, the amount of crystal seed was 4g. When the PEG was 400ppm, the average particle size and liner crystal growth rate of $CaSO_4$·$2H_2O$ were both largest.

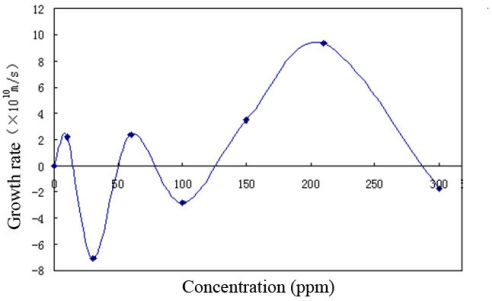

Fig. 6. $CaSO_4$•$2H_2O$ crystal growth rate diameter distribution with the addition of $K_2Cr_2O_7$.

4 Conclusion

In this paper, solubility of calcium sulfate dihydrate in gypsum type brine system was developed. Potassium dichromate, PEG and SDBS were chosen as additives to study the crystallization kinetics of calcium sulfate dehydrate in gypsum type brine system. The results showed that line growth rate was promoted when the concentration of potassium dichromate was between 150ppm and 250ppm. The line growth rate of calcium sulfate dehydrate reached 9.333×10^{-10} m/s when the concentration potassium dichromate was 210ppm. PEG has an obvious effect on promoting the line growth rate of calcium sulfate dehydrate, it reached 2.057×10^{-9}m/s when the concentration of PEG was 400ppm, after that, it decreased with increasing the concentration of PEG. The line growth rate of calcium sulfate dehydrate increased when the concentration of SDBS was less than 300ppm, the line growth rate was 1.290×10^{-9}m/s when the concentration of SDBS was 30ppm.

Key words: gypsum type brine; calcium sulfate dehydrate; additives; crystallization kinetics; crystal growth.

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