Experimental study on preparation of α-hemihydrous gypsum by modification of desulfurized gypsum

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Abstract. In the process of preparing α-hemihydrous gypsum from desulfurized gypsum under atmospheric pressure, the optimum conditions of crystallization transformation and modification of desulfurized gypsum were studied. The effects of the type and concentration of composite salts (CaCl2, KCl, MgCl2 mixed solution) on the crystallization and modification of desulfurized gypsum were studied. The results were further verified by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC/TGA), so as to determine the ideal directional crystallization control index. The experimental results show that temperature, type and concentration of salt solution are the most sensitive factors in the crystallization process of desulfurized gypsum. The optimal control conditions for obtaining α-hemihydrous gypsum with good crystalline form are temperature 95℃~98℃, concentration of composite salt solution (CaCl2: MgCl2: KCl = 25:5:1) is 25%~30%, and slurry concentration is greater than 20%.

Keywords: Desulphurized gypsum; α-hemihydrate gypsum; modified;transcrystalline.

1. Introduction

At present, the State Electric Power Company has identified the wet limestone/gypsum desulfurization process as the main process of flue gas desulfurization in thermal power plants, and the waste residue produced by the desulfurization process is desulfurized gypsum (FGD). Lime wet desulfurization process is widely used because of its relatively mature technology, high desulfurization efficiency, wide source of raw materials, low cost and easy to obtain [1-3].

Desulphurized gypsum has a low application level and low added value due to its complex composition. At the same time, harmful substances in gypsum pollute the environment due to accumulation treatment, causing serious damage to the ecology [4,5]. The main component of desulphurized gypsum is calcium sulfate dihydrate, and the preparation of calcium sulfate hemihydrate by desulphurized gypsum can not only solve the utilization problem of desulphurized gypsum, but also greatly reduce the cost of preparing calcium sulfate hemihydrate [6].

In this paper, α-hemihydrous gypsum was prepared from desulfurized gypsum by means of recrystallization and modification with salt solution under atmospheric pressure. A series of comparative tests were conducted to study the effects of salt solution concentration, reaction temperature and time, slurry concentration and other factors on the product morphology of α-hemihydrate desulfurized gypsum, so as to determine the ideal directional crystallization control index for preparing α-hemihydrate desulfurized gypsum.

2. Experimental

2.1 Materials.

The desulfurized gypsum used in this experiment comes from the local power plant, and its chemical composition is shown in Table 1. The reagents used, CaSO4・2H2O, CaCl2, MgCl2 and KCl, are all chemically pure.

Table 1 Chemical composition of desulfurized gypsum wt%

CaO	SiO_2	MgO	Al_2O_3	SO_3	Fe_2O_3	Free water
30.76	2.23	0.77	1.96	43.76	0.04	18.65

2.2 Methods.

The operating temperature range of this experiment is preset to be 80℃~98℃. At the beginning of the experiment, the proporpropored crystalline mother liquor was added to the three-mouth flask, heated to the pre-set temperature, and a certain amount of 50g FGD gypsum sample was slowly added after it stabilized for 0.5hr. The stirring speed of the agitator is controlled at about 150rpm.

3. Results and discussion

3.1 Effect of concentration of complex salt solution on transformation of FGD gypsum crystal

The result is shown in Figure 1. The experimental conditions were 95℃ and the ratio of composite salt solution was CaCl2: MgCl2: KCl= 25:5:1.

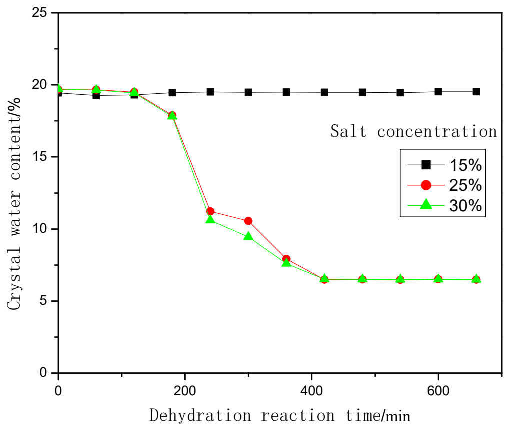

Fig. 1 Effect of the concentration of complex salt solution on the conversion process of FGD gypsum crystal

As can be seen from Fig. 1, when the concentration of composite salt solution is 15%, there is still no crystallization change in dihydrate gypsum even after 5 hours of reaction. When the concentration of composite salt solution increased to 25% and 30%, the content of crystal water of FGD gypsum decreased from 20% to 5%~7% within 2 hours, indicating that FGD gypsum transformed into a new gypsum phase.

3.2 Effect of temperature on the transformation of FGD gypsum crystals

The result is shown in Fig. 2. The mixed salt solution is 30%.

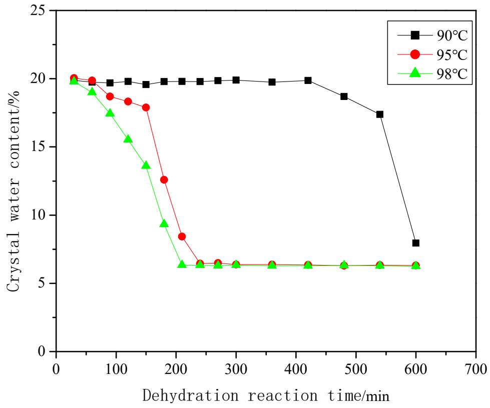

Fig. 2 Effect of temperature on the transformation of FGD gypsum crystals

As can be seen from FIG. 2, when the FGD gypsum in the composite salt solution is stirred in the reactor for 10 hours at a lower temperature of 90℃, crystallization will occur. At 95℃, the FGD gypsum in the reactor was stirred for 200min, but the crystallization rate was relatively slow. However, at 98℃, the crystal water content of FGD gypsum solid sample in mixed salt solution decreased from 19.9% to about 7.5% within 150min, and the crystallization rate was very obvious.

It can be seen that temperature is an important factor in the crystallization and modification of FGD gypsum, and the temperature range of 94℃~98℃ is the key to the crystallization of FGD gypsum in composite salt solution. The electron microscope scanning results of 95℃ and 98℃ samples are shown in Fig. 3 and Fig. 4.

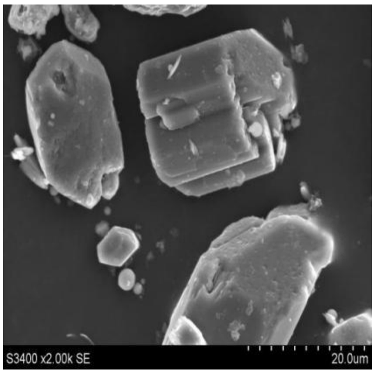

Fig. 3 Sample scan at 95℃

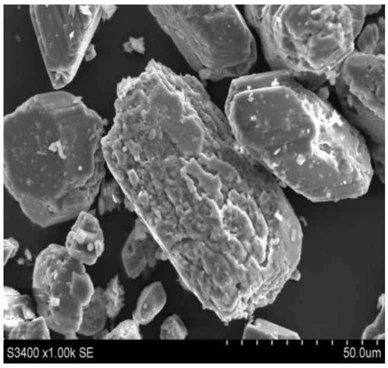

Fig. 4 Sample scan at 98℃

Fig. 3 and Fig. 4 show that the crystallization effect of FGD gypsum at 95℃ is better than that at 98℃. According to the crystal growth theory, the formation of this situation is due to the fact that at high temperatures, the ability of crystalline particles to repel foreign impurities is greatly enhanced, and the quality of the crystal will be better than that of the general low-temperature growth, but if the temperature is too high, a large number of crystal nuclei will be produced, and the nucleus is centered and enriched, and the result cannot guarantee the full growth of the generated crystal, thus forming an unsatisfactory crystal.

3.3 Effect of slurry concentration on the transformation of FGD gypsum crystals

The result is shown in Fig. 5.

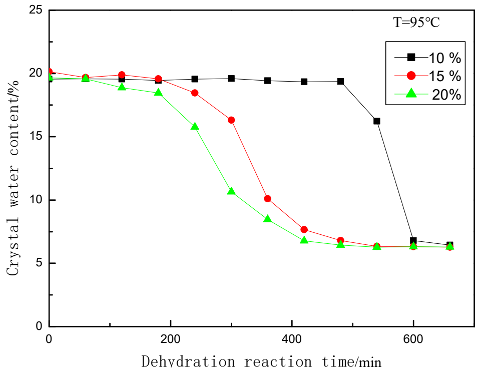

Fig. 5 Effect of slurry concentration on the transformation of FGD gypsum crystals

As can be seen from Figure 5, when the slurry concentration is 10%, the gypsum phase conversion process takes 8hr, when the slurry concentration is 15%, it only takes 5~6hr, and when the slurry concentration reaches 20%, the conversion process is shortened to 4~5hr.

3.4 DSC/TG analysis of newly formed gypsum phase

The result is shown in Fig. 6.

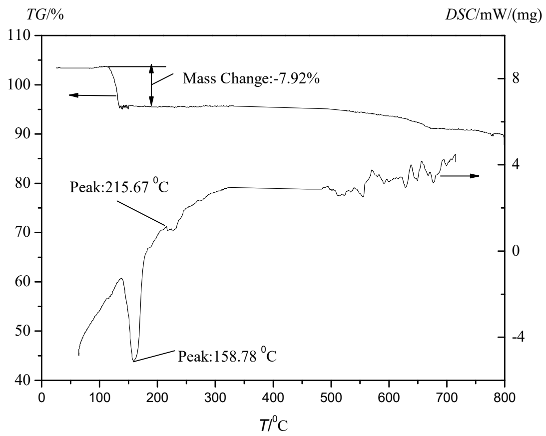

Fig. 6 DSC/TG diagram of newly formed gypsum phase

The theoretical heat release peak of α-hemihydrous gypsum appears near 220℃ [7]. According to the analysis in Fig. 6, the crystal water content of the generated gypsum phase is 7.92%, and the sample begins to lose weight when heated to 109℃, resulting in endothermic valley. At the end of weightlessness, a small exothermic peak began to appear, and the position of the exothermic peak was 215.67℃. According to the characteristics of DSC thermal analysis curves of hemihydrous gypsum phases, it can be concluded that α-hemihydrous gypsum is transformed from FGD gypsum in composite salt solution at 95℃.

4. Conclusions

The type and concentration of salt, temperature and slurry concentration can affect the crystallization of FGD gypsum. When the concentration of the composite salt solution is 25%-30%, the temperature is 95 ℃~98 ℃, and the slurry concentration is greater than 20%, the ideal α -hemihydrous gypsum can be obtained. The thermal analysis by SEM and DSC shows that the generated gypsum is α -hemihydrous gypsum.

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