

Modification of FGD gypsum in hydrothermal mixed salt solution

WU Xiao-qin², WU Zhong-biao^{1*}

(1. Department of Environmental Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: zbwu@zju.edu.cn; 2. Department of Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China)

Abstract: A novel utilization way of the sludge from wet calcium-based flue gas desulfurization (FGD) processes has been developed in this paper. This study focused on the conversion of the FGD gypsum into α -hemihydrate calcium sulfate by a hydrothermal salt solution method at atmospheric pressure. Experimental study has been carried out in a batch reactor. Qualitative and quantitative analyses were made by DSC/TG thermal analysis, SEM, XRD, metalloscope and chemical analysis. The experimental results showed that the modification of FGD gypsum was controlled by the dissolution and recrystallization mechanisms. With the introduction of FGD gypsum the salt solution was supersaturated, then crystal nucleus of α -hemihydrate calcium sulfate were produced in the solution. With the submicroscopic structure of FGD gypsum crystal changed, the crystal nucleus grew up into α -hemihydrate calcium sulfate crystals. Thus, the modification of FGD gypsum was fulfilled.

Keywords: FGD gypsum; modification; hydrothermal mixed salt solution; atmospheric pressure

Introduction

Wet calcium-based flue gas desulfurization (FGD) is the most common method for the reduction of sulfur dioxide emission from combustion of fossil fuels. However, large quantities of FGD scrubber sludge, containing sulfate-and/or sulfite-rich, are generated during this FGD process. Traditional method of FGD gypsum disposal ends up in landfill, which not only occupies a plenty of land source, but also initiates environmental recontamination. Therefore, environmentally friendly and economical disposal of the sludge is of great importance to FGD industry with well development (Makkinejad and Hildemar, 1991; Heiner, 1997; Steffan and Golden, 1991).

It is possible that FGD sludge can be used to produce commercial gypsum (namely FGD gypsum) with good quality. The products of FGD gypsum consist of wallboard, plaster, cement, road base construction, mining mortar, soil amendment, and so on (Täubert, 1991; Venta, 1991; Steffan and Golden, 1991). The property of FGD gypsum results in its ability to be transformed into various products, which are dihydrate calcium sulfate (DH), hemihydrate calcium sulfate (HH), and anhydrate calcium sulfate (AH). Davis (French Gypsum Industrial Institute, 1987) found that gypsum could be changed into α -HH in boiling water at atmospheric pressure. In that process, temperature was one of the most sensitive factors for recrystallization and growth of α -HH. And the transition rate of FGD gypsum increased with an increase of temperature. α -HH is a gypsum material of high intensity, which is used aboard in the fields of

machine, shipping, building materials, and so on. So α -HH tends to become a prominent issue because of its outstanding properties (Ding, 1992, 1993; Wang *et al.*, 1999). Donald (1996) and Tong (1996) also studied on α -HH produced from FGD sludge and concluded that it was feasible for FGD sludge to be modified as α -HH, which not only improved the quality of FGD sludge, and also increased the economic profit and decreased the FGD cost. Therefore how to modify FGD gypsum to produce α -hemihydrate calcium sulfate appears to be a choice. Unfortunately, not much valid information on whether and how it works is available so far.

1 Experimental apparatus and procedure

There are two basic approaches to obtain α -HH from FGD gypsum. One is the conversion under high pressure in an autoclave, which is subdivided in dry and wet methods. And the other is in salt solution at atmospheric pressure or acid solution at reduced vapor pressure. However, hydrothermal process is the most adequate one for producing α -HH from FGD gypsum (Tong and Shen, 1996; Tong and Xi, 2000). In this study, the experiments of a direct conversion from FGD gypsum into α -HH were carried out.

Experimental process was carried out in a three-neck flask with a volume of 500 ml. A thermostat with an electromagnetic constant speed stirrer with 50-100 r/min was used to provide uniform heat and agitation for slurry (Fig.1) and FGD solid was suspended in an aqueous mixture comprising the ingredients defined in Table 1. Fig.2 shows the sandwich structure of gypsum, which is composed of

calcium and sulfate ions layers crossing with water molecule layer.

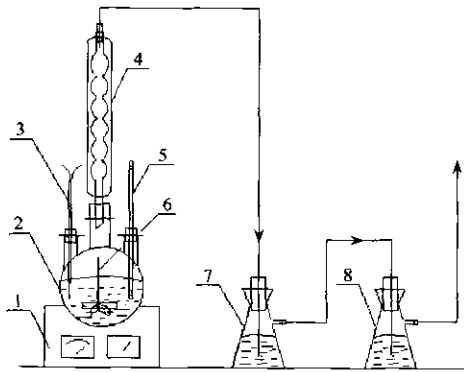


Fig.1 Batch apparatus for calcium sulfate modification

1. thermostat; 2. three-neck flask; 3. electrode; 4. global condenser; 5. thermometer; 6. electromagnetism stirrer with a controlled speed; 7, 8. tail gas absorber

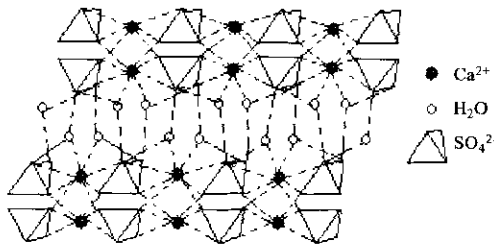


Fig.2 Sketch of gypsum structure

Table 1 Ingredients of the media

Composition of the media, wt%				
Salt solution concentration	Modifier	Crystal seeds	Stable agent	Slurry concentration
8—30	0—1	0—1.0	0.5—1.5	5—25

At the beginning of the experiments, salt solution was heated around 80—90°C and pH value was adjusted by adding either acid or more FGD solid. Temperature was sequentially raised to the preset value and kept constantly. Then FGD gypsum was put into the flask. After that the mixture was kept at this temperature until the α -HH crystals grew up into desired size and required purity.

Before experiments, pH value and combined water content of raw materials were measured. Samples of modified crystals were also taken and treated orderly for each run. The pH value of raw materials was measured in slurry of 5% solid content, which was stirred for 5 min. 20 g of raw materials was dried in a convection oven at 45°C for 15 h until constant weight to get rid of free water, then burnt in muffle at 350°C for 3 h to obtain the combined water content (Venta, 1991). In each run, the samples were treated by filtering, washed by hot water, fixed by 10 ml acetone, dried at 45—90°C until reaching a

constant weight, and finally stored in crucible for combined water analysis. Moreover, crystal phase and shape were determined by DSC/TG thermal analysis (NETZSCH STA 409 Luxx, Germany), SEM (HITACHI S-570, Japan), XRD (D/max-RA, Japan), and metaloscope with polarized light (XLP-6/6A, Chongqing Optical & Electrical Instrument Co., Ltd.). SEM and XRD were accomplished by center of analysis and measurement of Zhejiang University. And thermal analysis was fulfilled in laboratory under the condition of temperature rising speed of 5°C/min.

2 Results and discussion

2.1 Raw materials and modified crystals

The FGD gypsum used in experiments was taken from a power plant in Hangzhou. The results of chemical analysis for FGD gypsum were given in Table 2 (Cong *et al.*, 1997). Sulfate is the major component in the sludge solid, while the sludge solid also contains some sulfite, carbonate, soluble and insoluble matter. According to the analytic results, the particle size distribution is shown in Fig.3 for the raw materials. The geometric mean diameter is about 23.75 μm , and the specific surface area is 0.253 m^2/g . The pH value of raw materials is 6.75, and the combined water content is 20.05%, which is very near to the theoretical value(20.92%).

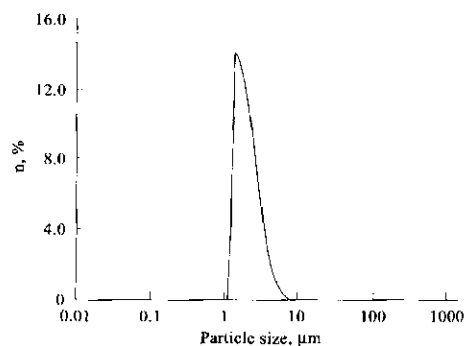


Fig.3 Particle size distribution of raw materials

Table 2 Results of chemical analysis of FGD gypsum solid (wt%)

Free moisture	CaO	SiO ₂	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	MgO	Loss
10	31.5	4.3	1.73	41.1	1.15	1.30	17.2

SEM photos show that raw materials are irregular crystals, while modified crystals are regular columnar crystals with larger size (Fig.4). According to the international standard databases of XRD graphs and DSC/TG graphs of different gypsum phases, analytic results from XRD and DSC/TG indicate that the modified crystals are mainly α -HH(Fig.5 and Fig.6).

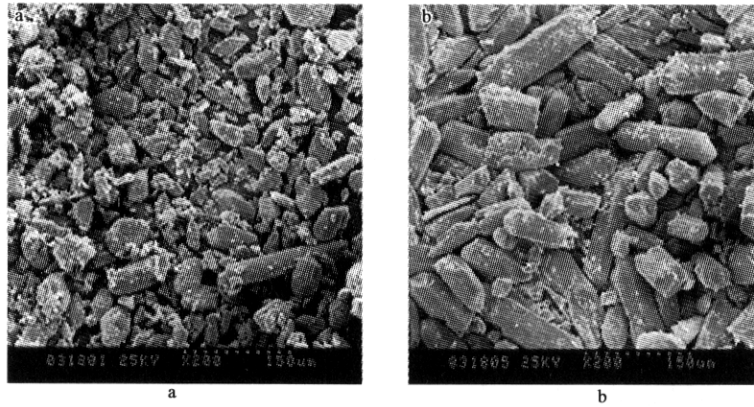


Fig.4 SEM photo of raw materials(a) and modified crystals(b) from FGD gypsum

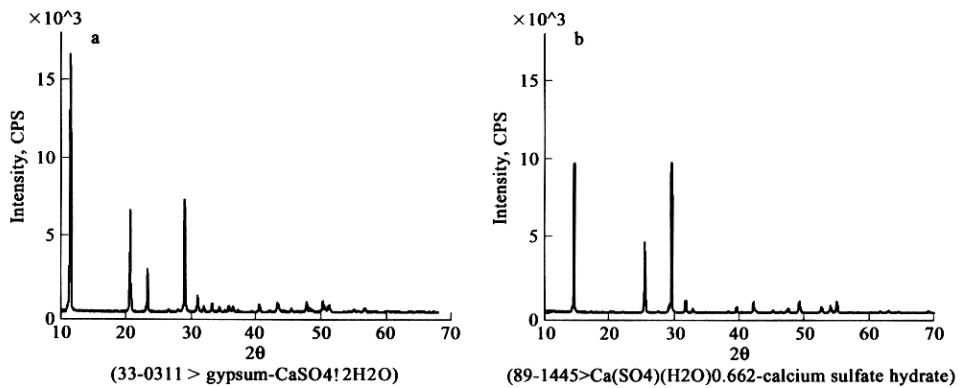


Fig.5 XRD graph of raw materials(a) and modified crystals(b)

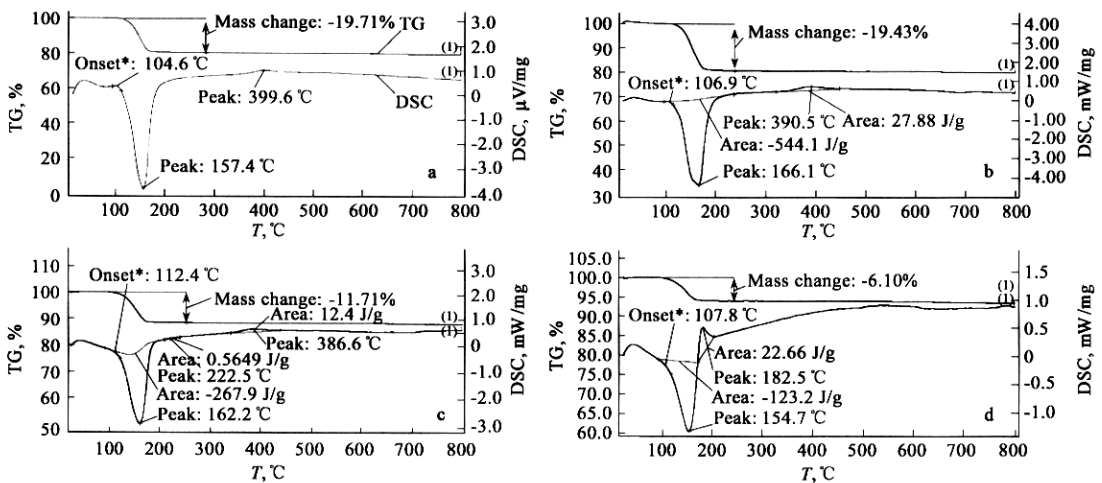


Fig.6 DSC/TG graph of raw materials(a); gypsum sample at 120 min(b); gypsum sample at 210 min(c) and modified crystals(d)

2.2 FGD gypsum modification by hydrothermal method

The quality of FGD gypsum modification is affected by the experimental operating factors. Of these factors, temperature and mixed salt solution concentration are the key factors, then the solid content in slurry and pH value.

2.2.1 Temperature

In the experiments, crystallization reaction lasts

for 11 h, FGD gypsum still keeps the same combined water content as raw materials in the range of low temperature ($< 80^{\circ}\text{C}$). In the range of middle temperature ($80\text{--}98^{\circ}\text{C}$), the transition happens after 10 h, while only 4 h when temperature is more than 98°C . In the range of high temperature nearly to boiling point of water, the recrystallization will appear very fast after around 20 min reaction (Fig.7). At different temperatures, the shapes of crystals observed under

metalloscope by polarized light are different. The metalloscope photos of raw materials and modified crystals at different temperatures are shown in Fig.8. At middle temperature range, the modified crystals are regular stubby columnar crystals. At boiling point, the crystals look like regular fine needles.

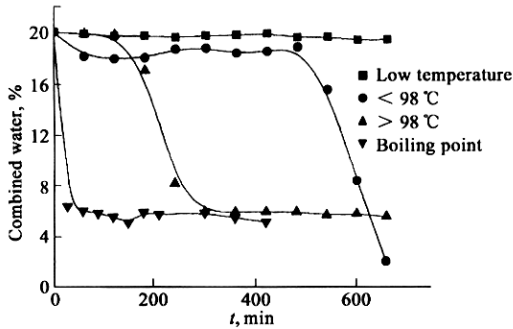


Fig.7 Relation of combined water and time at different crystallization temperatures

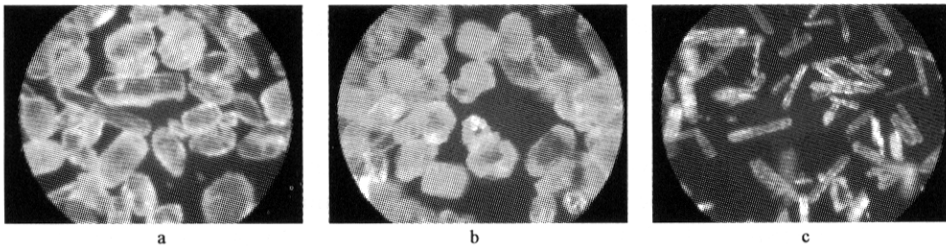


Fig.8 Metalloscope photos of crystals at middle and high temperature
a. raw materials; b. modified crystals at middle temperature; c. modified crystals at high temperature

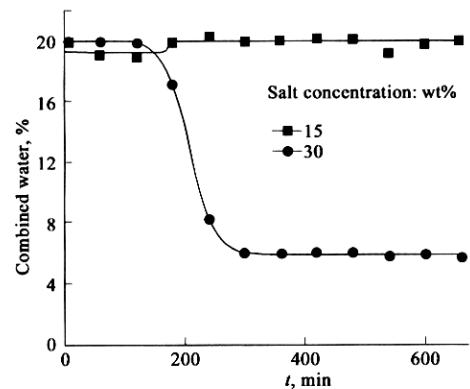
supersaturated solution of calcium sulfate is formed within a short time, and then a plenty of α -HH crystal nucleus are produced. Hence, it reduces the calcium sulfate concentration in the solution leading to an increasing of mass transfer resistance between solution and crystal surfaces. Thus, it is benefit to the formation of the fine crystals at high temperature(over than 98°C).

2.2.2 Salt solution concentration

Salt solution concentration is another key factor of FGD gypsum modification. The solution consists of alkaline and alkaline-earth metals solution, of which alkaline halide and hydroxide are the most effective components. The crystals shape becomes uniform and regular by modification (Fig.8). Only appropriate salt concentration can assure the recrystallization of FGD gypsum. The recrystallization rate of gypsum is accelerated greatly at a high level of salt solution concentration, and the shape of the crystals is also decided. One reason is that the boiling point of solution at high concentration is higher than that at low concentration (Fig.9). The other is that different ions in the mixed salt solution can be adsorbed

According to experimental results, the temperature of recrystallization reaction not only affects the phase transition of gypsum, but also is a key factor of the gypsum phase growth mechanism. Generally, gypsum crystals growth is divided into two phases. It obeys the growth mechanism of superficial control when the temperature is less than 98°C , while diffusion control when temperature is more than 98°C . For calcium sulfate, the solubility has negative relationship with temperature within the range of temperature investigated. So it is easy to obtain the supersaturated solution of calcium sulfate for HH. In the range of temperature 80 — 98°C , gypsum phase transition appearing as α -HH crystal nucleus is produced slowly, so α -HH crystals have enough time to grow up. Finally stubby columnar crystals come into being. However, when experimental temperature is more than 98°C , especially at boiling point, the

selectively in the different crystal surface, which changes the relative growth rate of different crystal surfaces.



particles will deposit at the bottom of flask with the increasing of crystal size. Hence, it will be removed very fast. The induced process lasts about 7 h at low solid content, while about 2 h at a high level of solid content. The recrystallization rates increase with an increasing in the solid content. It is because solid content in slurry influences the stability of supersaturated solution during FGD gypsum modification. Actually, high solid content in slurry can reduce the width of crystallization metastable zone, which results in the instability of supersaturated solution. Thus it is suitable for FGD gypsum to be modified at high solid content in slurry.

2.2.4 pH value

pH value has lesser effect on the process of gypsum recrystallization, but primarily on the crystals shape. Fig.10 shows that the crystals shape is changed from acicular to stubby when pH value varies from 4.0 to 8.0. In acidic pH value range, recrystallization can be accelerated by the residual hydrogen ions after digesting FGD gypsum solid. It is interesting that stubby columnar crystals can be steadily produced in the salt solution at pH value between 6.0 and 8.0. However, the time needed for modification increases with an increasing in the pH value of slurry.

pH value indicates the hydrogen ion concen-

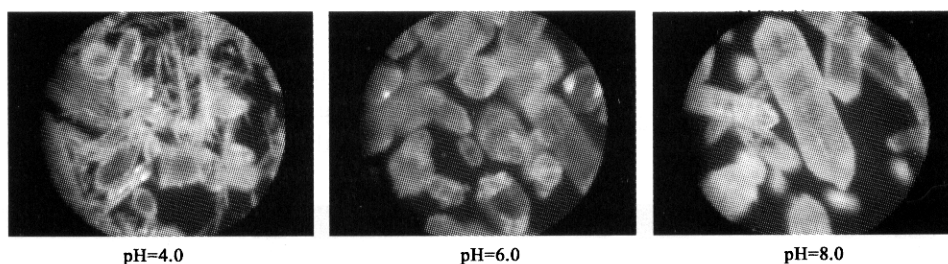


Fig.10 Crystalline shapes of modified crystals at different pH value

tration in solution. In the system of FGD gypsum modification, hydrogen ion can be regarded equivalently as M^{2+} , which exists as $H_3(H_2O)^{3+}$ in the solution. Usually, $H_3(H_2O)^{3+}$ will be adsorbed on the columnar surface of gypsum crystals. The adsorption of $H_3(H_2O)^{3+}$ brings a dilute effect on the columnar surface of gypsum crystals, which can resist mass transfer of Ca^{2+} and SO_4^{2-} from solution to the columnar surface. So the growth of crystals columnar surface slows down, and acicular crystals are produced. With an increasing in pH value, the effect is reduced and crystals shape is modified.

2.3 Mechanism

According to experimental results and discussion, temperature and mixed salt solution are the key factors of the modification of FGD gypsum. These two factors influence primarily the physicochemical properties of calcium sulfate phases in water, which results in the transition of FGD gypsum from DH to α -HH.

During FGD gypsum modification, FGD gypsum dissolves firstly in hydrothermal mixed salt solution. The concentration of calcium sulfate solution is controlled not only by temperature but also by salt solution concentration. Meanwhile, temperature also assures the phase transition point of different gypsum phases. On the one hand, the solubility of DH increases until the temperature is over than $42^\circ C$, and then decreases with an increasing in temperature. The solubility of HH decreases with rising temperature. On

the other hand, mixed salt solution has high solubility and heat transfer coefficient, which improve FGD gypsum dissolution. According to the equilibrium relationship of different gypsum phases (Fig.11; Liu, 1999), there is an important intersection: DH intersects with HH at $98^\circ C$. The solubility difference between DH and HH let the transition from DH to HH become possible. So it is benefit to form supersaturated solution for HH in hydrothermal mixed salt solution within experimental temperature range investigated. The HH crystals nucleus can be produced in the solution preferentially. However, the solubility of α -HH is less than that of β -HH, so the nucleus are α -HH crystal nucleus and the modified crystals is α -HH. Thus, the modification of FGD gypsum is fulfilled.

Besides the equilibrium and solubility of different gypsum phases, the mixed salt solution also has effect on the superficial vapor pressure of water on the calcium sulfate solution. The relations between the superficial vapor pressure of water, DH, and salt solution are showed in Fig.12 (Jorg, 1991). In mixed salt solution, different cationic ions have different effect on the reduction of partial pressure of water, which corresponds to the lift of boiling point of the media. For example, the calcium ion-containing media have higher boiling point than magnesium ion-containing media at the same level of concentration. Therefore, as long as water is at

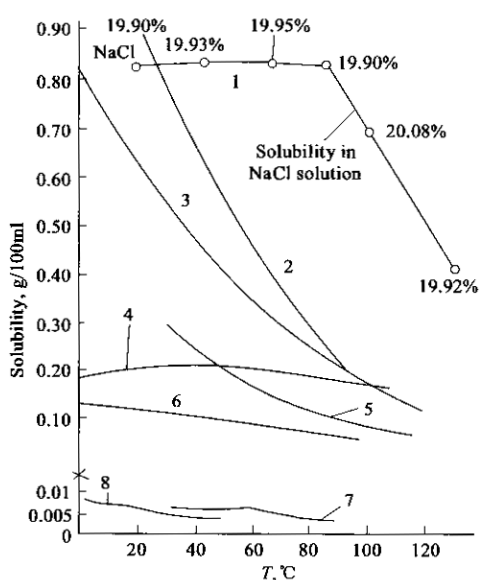


Fig.11 The solubilities of different calcium salt in water(Liu, 1999)
 1: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; 2: $\beta\text{-CaSO}_4 \cdot 1/2\text{H}_2\text{O}$; 3: $\alpha\text{-CaSO}_4 \cdot 1/2\text{H}_2\text{O}$; 4: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; 5: CaSO_4 ; 6: $\text{Ca}(\text{OH})_2$; 7: $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$; 8: CaCO_3

atmospheric, the boiling point of salt solution should be more than that of the water, which is equivalent that a high pressure acts on the water surface leading to an increasing of the boiling point just as an autoclave utilized. So mixed salt solution is also in favor of FGD gypsum modification by changing the superficial vapor pressure of the solution. Moreover, the shape of modified crystals is decided by selective adsorption of different ions in the mixed salt solution on different surfaces of gypsum crystals.

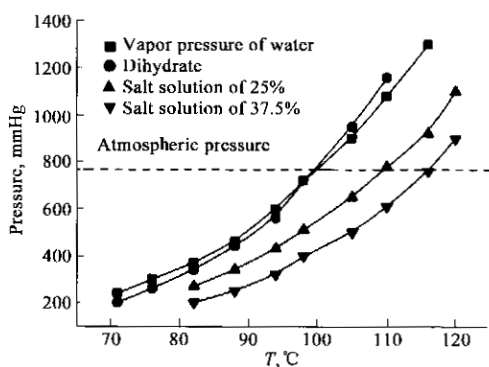


Fig.12 Graphs of vapor pressure of water, dihydrate and salt solution(Jorg, 1991)

3 Conclusions

FGD gypsum can be modified successfully from DH to α -HH in hydrothermal mixed salt solution at atmospheric pressure. According to experimental results, the optimal ranges of operating factors are: (1) temperature range is 90–98°C; (2) the concentration of mixed salt solution is 20%–30%(wt%); (3) the solid content in slurry is 10%–20%(wt%), and (4) pH

value is 6.0–8.0. Of the factors, temperature and mixed salt solution are the key factors. They influence the physicochemical properties of gypsum phases, which results in the process of gypsum dissolution and recrystallization. In experiments, α -HH is the dominant product in the mixed salt solution. Moreover, the modified crystals are stubby columnar crystals. The matter redistribution of calcium sulfate is accomplished, and the modification of FGD gypsum is fulfilled.

References:

- Cong G, Xing S, Zhang H, 1997. Study on the properties of FGD gypsum[J]. *New Building Materials*, 12: 10–12.
- Ding Z, 1992. Hemihydrate gypsum preparation (1)[J]. *Non-Metallic Mines*, 6: 56–58.
- Ding Z, 1993. Hemihydrate gypsum preparation (2)[J]. *Non-Metallic Mines*, 1: 57–60.
- Donald W K, Tong S, 1996. Process for production of alpha hemihydrate calcium sulfate from flue gas sludge [P]. US Patent, October, 8, 1996.
- French Gypsum Industrial Institute, 1987. Gypsum [M]. Beijing: Architecture Industry Press.
- Heiner H A M M, 1997. FGD gypsum utilization: the role of European gypsum industry(1)[J]. *Building Artificial Boards*, 4: 33--35.
- Heiner H A M M, 1998. FGD gypsum utilization: the role of European gypsum industry(2)[J]. *Building Artificial Boards*, 1: 40–41, 43.
- Jorg B, 1991. Alpha hemihydrate in conjunction with the flue gas desulfurization of a power plant [C]. 2nd International conference on FGD and chemical gypsum. Toronto, Canada, May 12–15, 1991.
- Kuntze R A, 1993. Alpha plaster from FGD gypsum and potential markets [C]. 3rd International conference on FGD and chemical gypsum. Toronto, Canada, September 6, 1993.
- Liu T, 1999. Handbook of waste treatment technology-waste gas volume[M]. Beijing: Chemical Engineering Press.
- Makinejad N, Hildemar B, 1991. The variables affecting the production of commercial grade gypsum from the FGD process [C]. 2nd International conference on FGD and chemical gypsum. Toronto, Canada, May 12–15, 1991.
- Steffan P, Golden D, 1991. FGD gypsum utilization: survey of current practices and assessment of market potential [C]. 2nd International conference on FGD and chemical gypsum. Toronto, Canada, May 12-15, 1991.
- Tong S, Shen S, 1996. Study of α -hemihydrate gypsum preparation from wet flue gas desulfurization[J]. *Journal of Wuhan University of Science and Technology*, 19(1): 51–57.
- Tong S, Xi G P, 2000. Direct formation of alpha form plaster from FGD sludge in sulfuric acid solution [C]. *Promoting New Technology for 21st Century Harmonized with Nature, the international symposium of 40th anniversary of Kitami*, June. 85–90.
- Taubert U, 1991. Occurrence and recycling of FGD gypsum in Europe especially in the Federal Republic of Germany [C]. 2nd International conference on FGD and chemical gypsum. Toronto, Canada, May 12–15, 1991.
- Valimbe P S, Malhotra V M, 2002. Effects of water content and temperature on the crystallization behavior of FGD scrubber sludge[J]. *Fuel*, 81(3): 1297–1304.
- Venta G J, 1991. Utilization of chemical gypsum in Japan [C]. 2nd International conference on FGD and chemical gypsum, Toronto, Canada, May 12-15, 1991.
- Wang Z, Zou A, Li G, 1999. New development of high strength gypsum materials[J]. *New Building Materials*, (9): 47–48.