

**Study on Wet Flue-Gas Desulfurization (FGD) Process  
in a Thermal Power Plant using Salt Slurry from Brine Purification**  
Salt, safety and environment

**Key Words:** Brine purification, Salt slurry, Wet FGD, Organic acids

**Abstract**

In this work, the process of wet Flue-gas desulfurization (FGD) using salt slurry from brine purification in a thermal power plant was studied with a constant pH titration method. The effects of organic acids as synergistic agent on the desulfurization efficiency of the salt slurry and the quality of gypsum were discussed. The results show that the combination of the salt slurry with the organic acid synergist can be used as raw material for wet FGD in a thermal power plant. The new developed process can significantly improve the desulphurization efficiency ( $\eta$ ) with a value higher than 97.63%. Moreover, the quality of the by-product gypsum in particle size and purity can also be improved. The desulphurization process fully achieved the goal of waste-treatment with waste, energy-saving and emission-reduction, which greatly reduced the desulfurization cost of the thermal power plant with a high potential of widespread application.

**1.Introduction**

Brine purification, also called the pretreatment of brine, is one of the critical step during salt-making. The aim of the brine purification is to separate the ions such as  $\text{Ca}^{2+}$ 、 $\text{Mg}^{2+}$  from the raw brine before entering the heating chamber. The inorganic salts that are discharged in this process is termed as “salt slurry”.

Currently, salt slurry is usually landfilled as the waste by most companies, which leads to not only a waste of resources but also pollution of the natural and production environment. Therefore, developing advanced technologies for salt slurry treatment has become a common technical challenge in the domestic salt industry[1-3].

Wet limestone-gypsum desulfurization is the most mature technoly for flue gas desulfurization, in which the limestone or lime is used as the absorbent of sulfur. In this technology, the absorbent is mixed with water to form absorption solutions and then to spay in to the absoription tower to desulfur. The absorption solution is contacted and mixed with the flue gas, and the  $\text{SO}_2$  in the flue gas react with the solutions and the injected oxidizing-air to achieve the desulfur. The final product is gypsum.

The effective component of the salt slurry is mainly the precipitated calcium carbonate that is the same as limestone. This makes it feasible to use salt slurry as the raw materials for wet desulfurization. If the salt slurry that is produced in the process of brine purification can be used as the desulfurizer of FGD in the power plant, it will not only solve the problem related to  $\text{SO}_2$  pollution and the emission of the solid waste discharging to the environment, but also greatly reduce the production cost by using limestone as the desulfurization raw material [4-6].

Compared to using limestone as the absorbent in the wet FGD, the salt slurry in the wet FGD has poor activity and a slow dissolution rate. These are two main reasons limiting the rate of absorbing  $\text{SO}_2$  in the whole system. In general, the activity of the desulfurizer is used as one of the main parameters to measure the desulfurization efficiency. It has been proved from experiments that the higher the activity for the desulfurizer, the better it absorbs the  $\text{SO}_2$ . Under

certain conditions, it can significantly improve the absorbing rate of the salt slurry and boost its activity when some organic acids are added in the salt slurry solutions [7-8].

In this work, the constant pH titration method was used to study the wet FGD process, and the salt slurry was combined with organic acid synergists to improve the efficiency of the wet FGD and solve the problem of solid waste treatment of salt slurry.

## 2. Experiments

### 2.1. Instruments

A Type 835 constant pH titration apparatus (Swiss Wantong China Ltd.), LabX-6000 X-Ray Diffractometer (SHIMADZU International Trading Shanghai Co., Ltd), Nikon BASIC UNIT Microscopic imaging system (Nikon Instrument Shanghai Ltd.), HB-10 constant water bath (German Eika Equipment Co.), C-MAF HS 7 heating magnetic stirrer (German Eika Equipment Co.), BSA523 electronic balance (German Dolis Co. Ltd), and EMLA ultrasonic cleaning machine (German Aimar Equipment Ltd) were used in this work.

### 2.2. Raw materials

The materials used in this work include limestone powder (containing  $\text{CaCO}_3$  99.0 wt%, Sinopharm Chemical Reagent Co., Ltd), salt slurry from brine purification (containing  $\text{CaCO}_3$  92.0 wt%, Chinasalt Jintan Co., Ltd.), acetic acid (Analytical grade, Sinopharm Chemical Reagent Co., Ltd), citric acid (Analytical grade, Sinopharm Chemical Reagent Co., Ltd), benzoic acid (Analytical grade, Sinopharm Chemical Reagent Co., Ltd), adipic acid (Industrial grade, German BASF China Ltd), succinic acid (Industrial grade, German BASF China Ltd) and Malonic acid (Industrial grade, German BASF China Ltd).

### 2.3. Experimental process of constant pH titration

The finenesses of salt slurry and limestone are 250 mesh with 5% residue. In experiment, taking 250 ml of 0.1 mol/L  $\text{CaCl}_2$  solution with a measuring cylinder and add it to a beaker and Heating it in a water bath to a constant temperature of 50°C. Then, 1.50g salt slurry or limestone weighted with an electronic balance was added it into the beaker and stirred for 5 minutes with a rate of 800r/min.

According to the reference of the PRC electricity industry standards (The Determination of Reaction Rate of Limestone Powder for flue gas wet desulphurization - DL/T943-2005), a method to measure the activity of the salt slurry desulphurization was developed. The detailed method is described as follows: Putting the pH value electrode into the suspension solutions that is waiting for measuring, and the electrode should never touch the agitation blade. Setting the automatic pH titration at 5.5. Starting titrating with the hydrochloric solution of 1.0 mol/L and then timing. Recording the consumption of the hydrochloric acid at different times [9]. The consumption of the hydrochloric acid will be used to reflect the desulfurization activity of the salt slurry.

### 2.4. Industrial experiment process

The industrial experiment was conducted in three circulating fluidized bed boiler FGD devices with 75t/h in a power plant. The process flow sheet is shown in Fig.1.

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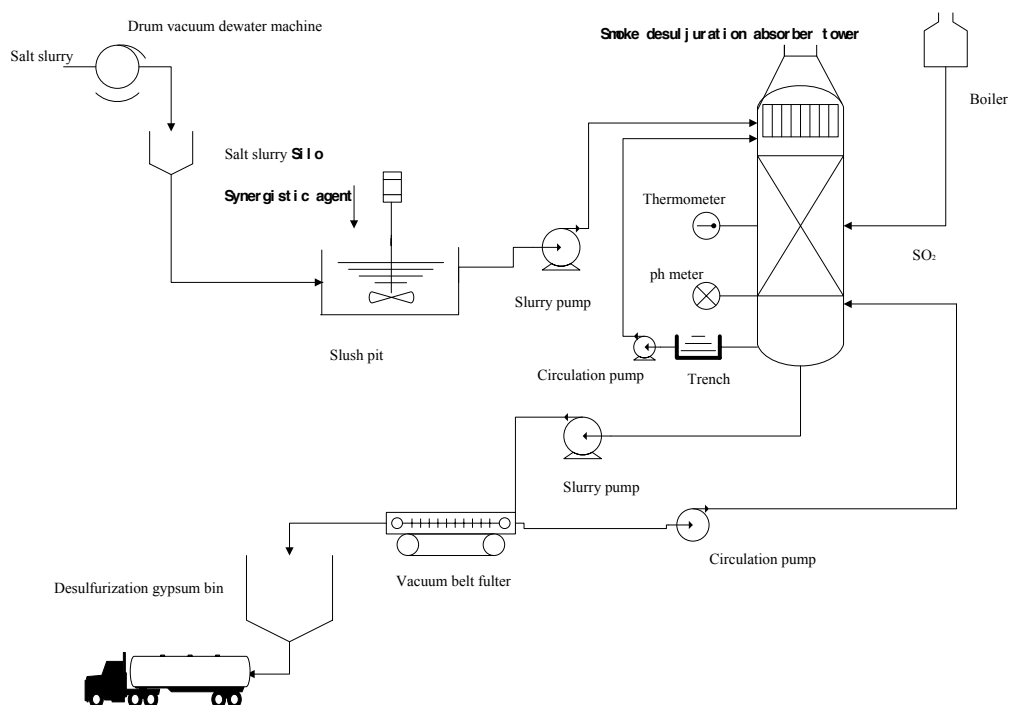


Fig.1. Process flow chart of salt slurry desulfurization system

## 3. Results and discussion

### 3.1. Characterization of physicochemical properties for the salt slurry

The structure of the salt slurry was characterized by XRD. The XRD results is depicted in Fig.2. As we can see from Fig.2, the values of  $2\theta$  at  $29.40^\circ$ 、 $35.90^\circ$ 、 $39.50^\circ$ 、 $48.51^\circ$  match with the crystal surface of  $\text{CaCO}_3$  (104)、(101)、(113)、(202) , while the values of  $2\theta$  at  $26.80^\circ$ 、 $27.50^\circ$ 、 $33.50^\circ$ 、 $38.20^\circ$ 、 $46.30^\circ$  match with the main crystal surface of  $\text{CaSO}_4$ . Therefore, we can conclude that the diffraction peaks of the salt slurry is mainly those forthe crystals of  $\text{CaCO}_3$  and  $\text{CaSO}_4$ .

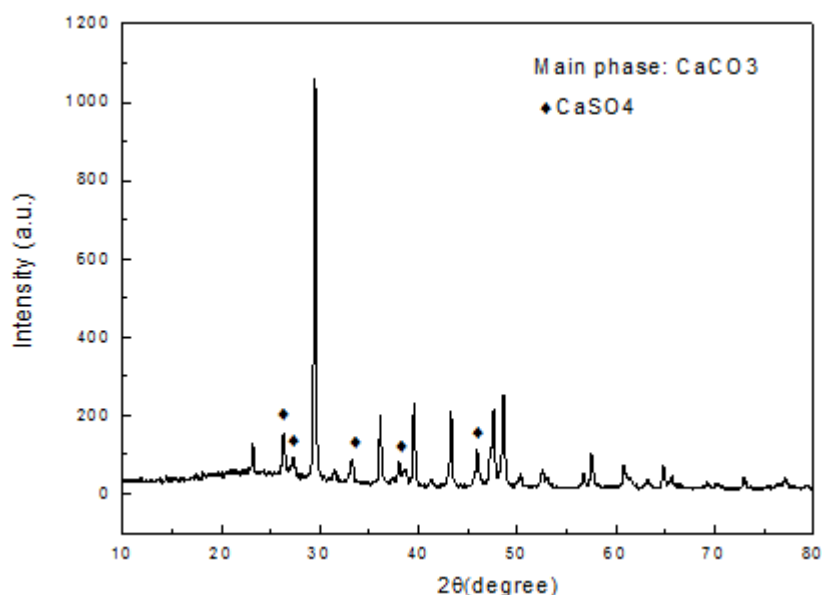


Fig.2. XRD of salt slurry from brine purification

The components in the salt slurry were analyzed by Energy Dispersive X-ray Spectrometry (EDS). The EDS map is shown in Fig.3. As illustrated in Fig.3, the components are mainly Ca, C and O with small amounts of S, Na, Mg, Al, etc. Therefore, the main contents of the salt slurry are  $\text{CaCO}_3$  and  $\text{CaSO}_4$  as well as a small amount of impurities such as magnesium hydrate, aluminium hydroxide and sodium chloride.

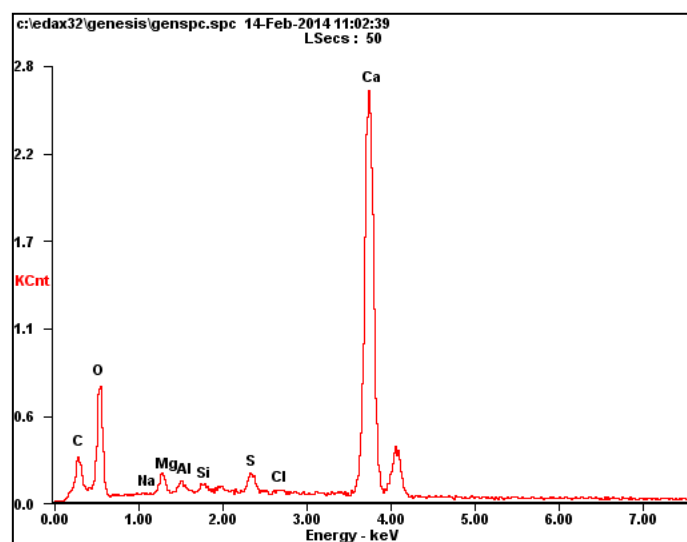


Fig.3. EDS of salt slurry from brine purification

### 3.2. Performance of salt slurry as desulfurization

3.2.1. Comparison of the desulfurization efficiency between salt slurry and limestone powder. Using the developed method, the desulfurization activities for the salt slurry and limestone, were tested, respectively. The results were compared with each other as illustrated in Fig. 4.

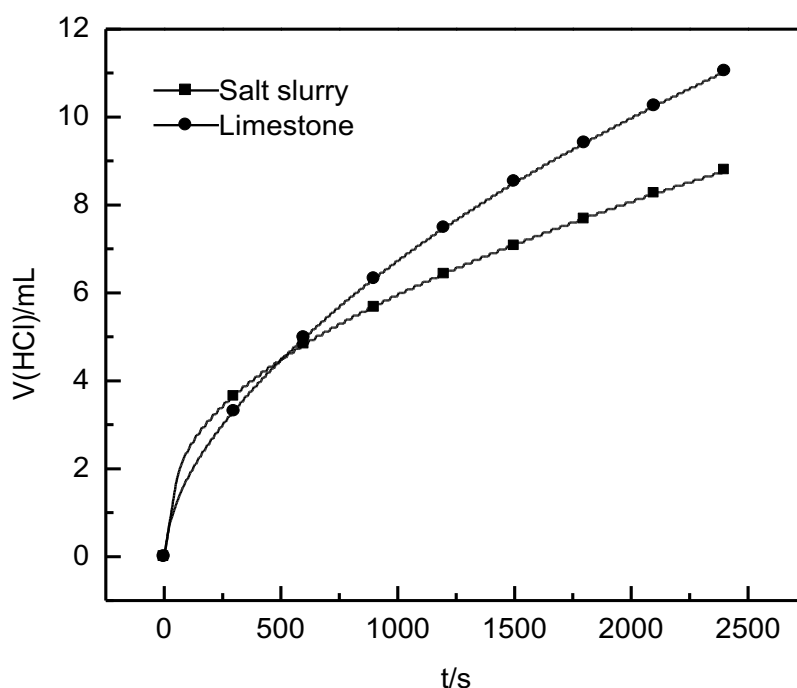


Fig.4. Wet FGD rate for the salt slurry and limestone

As we can see from Fig.4, the desulfurization activity for the salt slurry is lower than that of the limestone. Especially, after the medium process of the reaction, the activity is dropped significantly. The lower desulfurization for the salt slurry proves that the content of calcium carbonate in the salt slurry is lower than that in limestone. Meanwhile, the existence of the impurities such as magnesium hydrate, aluminium hydroxide and sodium chloride, especially the chloride ion in the salt slurry decrease the activity of the salt slurry, and subsequently decrease the desulfurization efficiency [3].

### 3.2.2. Influence of the organic acid synergist on the desulfurization efficiency of salt slurry

In order to improve the desulfurization activity for the salt slurry, different organic acid synergists were added into the salt slurry. The choice of the organic acid synergists was based on the good water-solubility, stability and low volatility, so that it can be used in the industry of desulfurization, and the added amount is 1% of the weight of salt slurry.

The desulfurization activities (i.e. the consumption of hydrochloric acid) for the salt slurry with added organic acid synergists were tested. The results are depicted in Fig. 5.

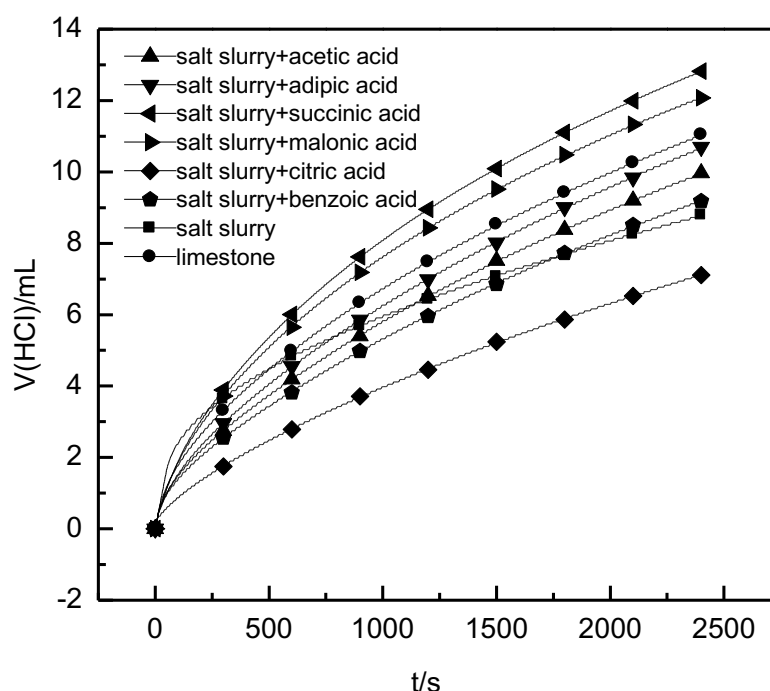


Fig.5. The consumption of the hydrochloric acid for the salt slurry with organic acid synergist

As shown in Fig.5, the consumption rate of the hydrochloric acid for limestone is significantly higher than the salt slurry without any additional organic acid synergists, which further proves that the reaction rate of limestone is much higher than that for the salt slurry. However, the consumption of hydrochloric acid for the salt slurry is greatly boosted after adding the other organic acid synergist except the citric acid and the benzoic acid. Especially after titrating to 1000s, the consumption rate has exceeded that for limestone, implying that the reaction rate of the salt slurry with organic acid synergist is higher than that of the limestone. This is because that the organic acid synergist can easily combine with  $\text{Ca}^{2+}$  and form the calcium organic acid, which can stimulate the dissolution of  $\text{CaCO}_3$  in the salt slurry and buffer the pH value of the absorbing slurry. The desulfurization efficiency of the salt slurry is improved, especially, in the middle and late period of time.

Besides, the addition of the organic acid synergist can greatly stimulate the dissolving of the salt slurry, which plays the role of pre-dissolving. The pre-dissolving makes that the total rate of dissolution is increased greatly. Meanwhile, the experiment results shows that most diprotic organic acids have better or positive effects. In view of the structure of the diprotic organic acids, the dissociation constant of  $K_{a1}$  is much higher than  $K_{a2}$  [10-12]. Since the carboxyl is the electron withdraw group with higher electronegativity, the other carboxyl can be easily dissociated. Meanwhile, the diprotic organic acids can buffer the pH value of the slurry absorption solution, and thus the pH value will not drop rapidly because of the dissolution of  $\text{SO}_2$  and eventually improve the desulfurization efficiency.

### 3.2.3 The influence of organic acid synergists on the desulfurization efficiency of the salt slurry at 1000s

4 organic acids with better performance were screened out according to the results shown in

Fig. 5. The desulfurization efficiency for the salt slurry with different dosage (0.1 – 2 wt%) of the acid but at the same time ( $t = 1000$  s) was further studied. The results are shown in Fig.6.

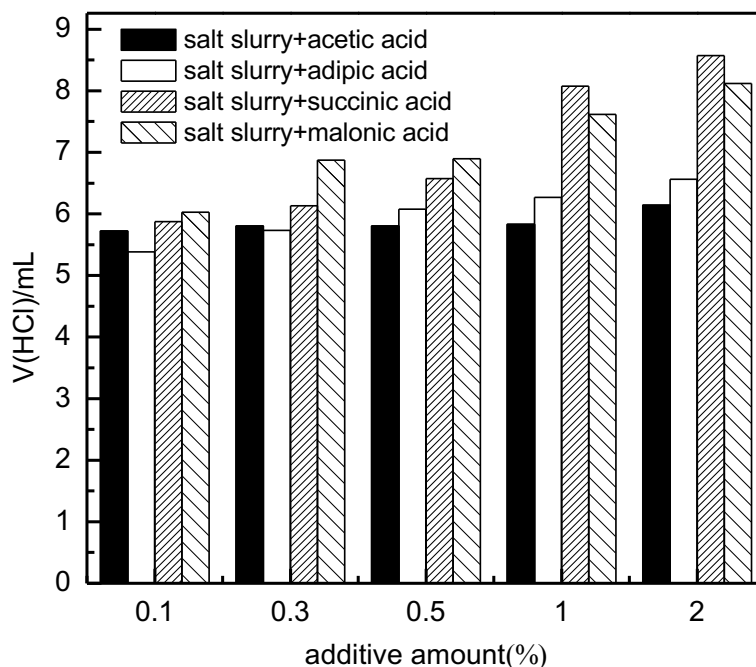


Fig.6. The consumption hydrochloric acid for the salt slurry with different dosages of 4 organic acids ( $t=1000$ s)

As we can see from Fig.6, the desulfurization efficiency can be improved to a certain degree when the addition amount of the organic acid synergist which takes up 0.3~1.0% of the weight of salt slurry. Especially, when the addition amount is 1.0%, the synergism of succinic acid and malonic acid is relatively more evident. All of these are related to the distance of two carboxyl of diprotic organic acids. However, when the addition amount is 2%, the performance tends to be stable, and thus the addition amount of the organic acid synergist should be controlled between 1% and 2%.

### 3.3. Industrial experiment of salt slurry desulfurization

#### 3.3.1. Desulfurization efficiency of the salt slurry with organic acid synergist

According to the previous experimental results and considering the stability, volatilization and the cost of the organic acid synergist as well as price, we chose the synergist with better activity to further investigate. By the industrial experiment, the formula of the synergist with good ability and moderate price were screened out.

Stirring the salt slurry with compound organic acid (1% weight of the salt slurry) and water, and then making the desulfurization absorbent slurry with 15% solid content, we carried out the desulfurization of the flue gas coming from three circulating fluidized bed boilers in one thermal power plant. The gas temperature was controlled at 145°C and the flow rate was controlled at 380,000 m<sup>3</sup>/h. In experiment, the results for the limestone desulfurization absorbent slurry were used as references. The efficiency of desulfurization is listed in Table 1.

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Chen Liuping, Cui Yaoxing and Leng Cuiting, Chinasalt Jintan Co., Ltd.

Name	time	SO <sub>2</sub> concentration before desulfurization (mg/Nm <sup>3</sup> )	SO <sub>2</sub> concentration after desulfurization (mg/Nm <sup>3</sup> )	Efficiency (η)
salt slurry	2016. 2	1345	76	94.30
saltslurry+formulaA	2016. 3	1332	29	97.83
saltslurry+formulaB	2016. 3	1348	26	98.07
saltslurry+formulaC	2016. 4	1386	30	97.84
saltslurry+formulaD	2016. 4	1428	25	98.25
saltslurry+formulaE	2016. 5	1395	33	97.63
reference	2016. 1	1393	43	96.91

Table1 Wet FGD efficiency of different desulfurization absorbent slurry  
reference: using limestone to prepare 15% slurry

The results show that the desulfurization efficiency can reach above 97% when using the salt slurry with 1% compound of the organic acid synergist as raw material, and all of them show a better desulfurization performance than the slurry with the same content of limestone. Among the salt slurry with synergist tested in this part, formula D behaves the best. Meanwhile, a slurry can be directly prepared based on different conditions of desulfurization, avoiding the treatment process of crushing and screening without any need to retrofit the desulfurization tower. In this case, we can not only achieve a better performance for wet FGD but also can the target of treating waste with waste combined with, energy-saving and emission-reduction, so that the salt slurry resources can be recycled.

### 3.3.2 Quality of gypsum after adding the organic acid synergist

Gypsum is the industrial by-product after desulfurizing in the thermal power plant and it has a wide range of applications. Table 2 is the comparison of different gypsum by using the limestone, salt slurry and the formula D synergist as the raw material of desulfurization. Fig.7 shows microimaging of the gypsum from the salt slurry after adding formula D synergist.

Gypsum Components	limestone	salt slurry	salt slurry + formula D
W H <sub>2</sub> O/%	28.76	33.04	21.64
W CaCO <sub>3</sub> /%	7.03	6.84	0.21
W CaSO <sub>4</sub> /%	44.82	42.23	65.68



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WCaSO <sub>3</sub> /%	14.17	13.68	6.94
WCl <sup>-</sup> /%	0.37	0.43	0.28
Wss/%	4.85	3.78	5.25

Table 2 The component analysis of the gypsum after using 3 different raw material for desulfurization

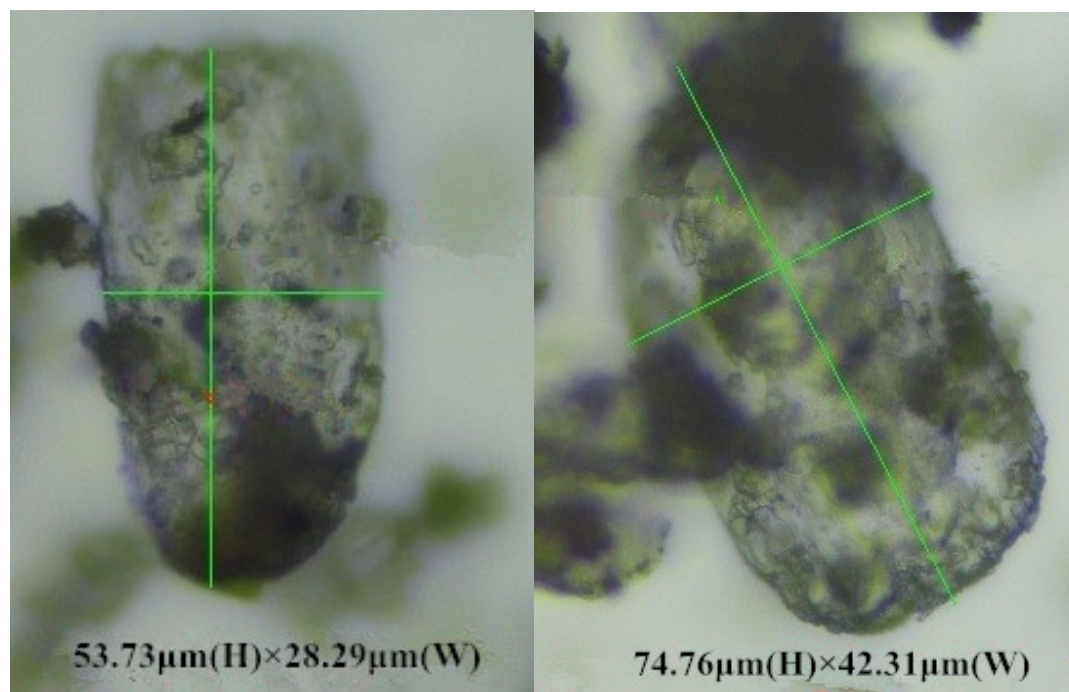


Fig.7. The particle size of the gypsum after adding organic acid synergist

According to the results listed in Table 2, we can find a significant decrease of the impurities such as calcium sulfite, calcium carbonate and chloride ion after adding synergist into the salt slurry. Meanwhile, the water content is decreased from 33% to 22%, and the calcium sulfite content is increased above 20%.

We can find the change of the particle size before and after adding the organic acid synergist into the salt slurry from Fig.7. Without adding synergist, the particle size of the gypsum is 53.73μm in length and 28.29μm in width, while after adding synergist into the salt slurry, the particle size is 74.76μm in length and 42.31μm in width. Therefore, the particle size is increased significantly when the organic acid synergist was added into the salt slurry. This also, which indicates that adding organic acid synergist into the salt slurry can greatly improve the availability of the raw material calcium carbonate. Meanwhile, it is also benefit for the intermediate product calcium sulfite to fully oxidize and for the slurry to dehydrate and then optimize the quality of the gypsum.

#### 4. Conclusions

In this work, using salt slurry from brine purification as sulfur absorbents in the desulfurization process (i.e. wet FGD process) was studied with the constant pH titration methods. It proves that by taking advantages of combining the salt slurry with the organic acid synergist, a new type of salt slurry as the raw material for wet FGD can be developed. The addition of some organic acids can greatly increase the desulfurization efficiency of the salt slurry.

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When the wet FGD is used in a thermal power plant, the desulfurization efficiency  $\eta$  can be higher than 97.63%, and the particle size and the purity of the desulfurization gypsum are obviously increased. If the desulfurization gypsum can be sold as the raw material, the comprehensive utilization of resources can be further enhanced. In addition, the total desulfurization system can run in long-term stability.

Besides, the application of wet FGD in power plant, on the one hand, solves the problem of slurry treatment for the salt industry by saving the cost of backfilling the slurry into the wells and recycling the salt slurry resources. On the other hand, it greatly reduces the desulfurization cost of the power plant, saving the consumption of limestone and protecting the resources. The research in this study achieves the target of treating waste by waste and the developed process has great potential for spreading and application.

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