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The Carbonation Behaviors of Limestone Particle in Oxygen-Fuel Circulating Fluidized Bed O₂/CO₂ Flue Gas

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ABSTRACT

Limestone powder is still applied as SO_2 sorbent in emerging oxygen-fuel circulating fluidized bed boiler, but its carbonation in O_2/CO_2 flue gas is an unclear problem. For a better understanding of carbonation behaviors, the tube furnace heating system was built for simulating circulating fluidized bed boiler flue gas by regulating the supply of O, CO_2, N_2, SO_2 and H_2O, and Carbonation reaction was tested. Thermal gravimetric analysis and scanning electron microscopy were used. It was found that carbonation is closely related to temperature, CO_2 concentration, impurities, water vapor, and cycle times; high temperature can promote carbonation process; high concentration of CO_2 can inhibit the chemical reaction stage speed of carbonation process, but it has little effect on the final conversion rate; water vapor can increase the final conversion rate of carbonation; the cycle times will reduce the activity of carbonation. The presence of carbonation turns the traditional boiler flue gas indirect desulfurization model into indirect desulfurization mechanism which does not have a negative impact on SO_2 removal efficiency.

Keywords: Oxygen-Fuel; Circulating Fluidized Bed; Limestone Particle; Carbonation; Desulfurization; Production Layer

1. Introduction

For many coal-fired power plants in China, limestone is widely used in dry desulfurization technology [1-4]. In traditional boilers, limestone (**Figure 1**) will be thermally decomposed into porous CaO particles (**Figure 2**) in high temperature flue gas, and then chemically react with SO_2 to produce $CaSO_4$. This type of SO_2 removal is called indirect desulfurization reaction [5-7], and the chemical equations are

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (1)$$

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow CaSO_4(s) \qquad (2)$$
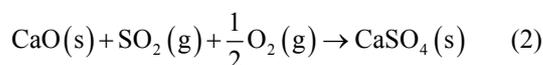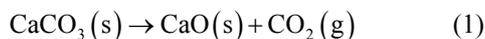
In fact, it may not be quite that simple for oxygen-fuel circulating fluidized bed (CFB) flue gas, because carbonation will happen at that carbon-dioxide-rich atmosphere. CaO carbonation is actually a reversible reaction about $CaCO_3$ calcinations [8] as shown in **Figures 3** and **4**. The phenomenon that limestone is partly calcined into
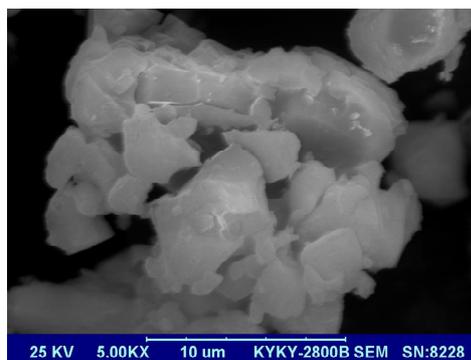
Figure 1. Unreacted limestone particle.

CaO does exist at the CFB oxygen-rich combustion zone where CO_2 concentration is lower and temperature is relatively higher, and when these CaO reach carbon-dioxide-rich zone it will present carbonation reaction [9]. In other words, these CaO will be finally reduced to $CaCO_3$ again at main flue zone where CO_2 concentration is >80% [10]. The chemical equation is

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad (3)$$
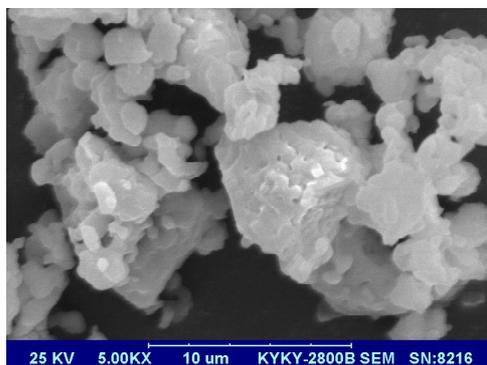
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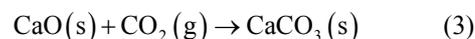
[*]Corresponding author.

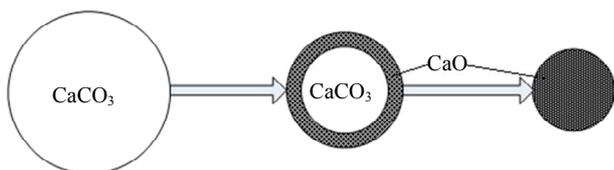**Figure 2. Porous calcined limestone particle.**

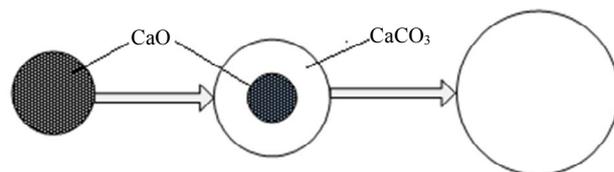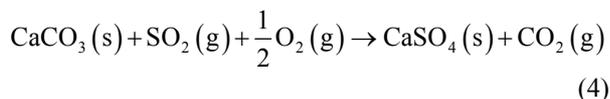

Figure 3. Limestone calcinations process.

Figure 4. Limestone carbonation process.

So in this case without porous CaO, limestone has to directly react with SO_2, which is called direct desulfurization [11-13], and the chemical reaction equation is

$$CaCO_3(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow CaSO_4(s) + CO_2(g)$$
(4)

Some discussions about carbonation can also be found in [14-21]. In order to find out the influence on carbonation from some physical parameters such as temperature, CO_2 concentration, water vapor, impurity, cycle times, we carried out a series of experiments on an altered tube furnace heating system. And this study also includes carbonation impact on the desulfurization process that is what we care about.

2. Experimental

The tube furnace heating system was rebuilt. Reactant gas distribution is a key for this investigation, so the piping system was set as shown in **Figure 5** for providing O_2, CO_2, N_2, SO_2, and H_2O. The partial pressure of every atmosphere is based on different type of experiment. O_2, CO_2 and SO_2 are reactant gas, and N_2 is a protective gas. Water vapor is one innovation which was suspected to definitely affect carbonation or desulfurization of lime-

stone in the flue gas. H_2O is injected by a pump into a heated pipe as shown in **Figure 5**. And **Figure 6** stands for Single channel syringe infusion pump and pipe heating system. The pump is LSP01-1A laboratorial pump which is single channel syringe infusion mode designed by Longer Precision Pump Co., Ltd., the acceptable syringe specification is from 10 μl to 60 ml, suitable for high accuracy and small flow rate liquid transferring. The thermocouple is to maintain the pipe wall above 200˚C to heat the water into steam in the main pipeline, and the steam flow is controlled by a solenoid valve. Powder samples are placed in a porcelain boat and pushed into the tube furnace, and any change of limestone on the porcelain is surveyed by the weight monitor for investigating calcinations/carbonation/desulfurization thermogravity (TG) law.

3. Effect on Carbonation from Temperature

In this section, 10 mg of limestone sample was weighed and token into the porcelain, and then it was heated up to 850˚C by 20˚C/min. For 10 minutes later, it was cooled down to different reaction temperatures by 20˚C/min. During above process, N_2 was always protective gas in order to avoid CaO being reacted. At different set temperature, the reaction atmosphere was switched to a mixed gas of CO_2 and N_2, and CO_2 concentration is 80%. The experimental results are shown in **Figure 7**. For every case, chemical reaction stage is fast and lasts about <1 minute, then the reaction rapidly approaches a slower state which is called product layer diffusion control stage.
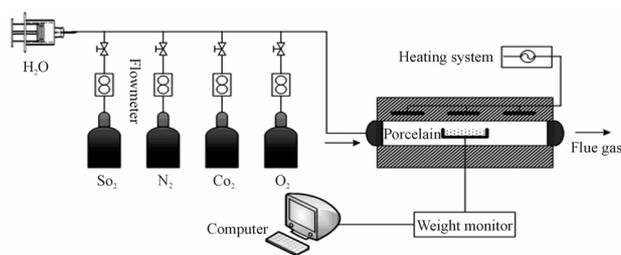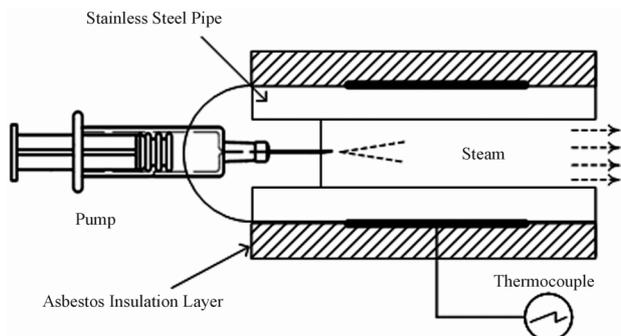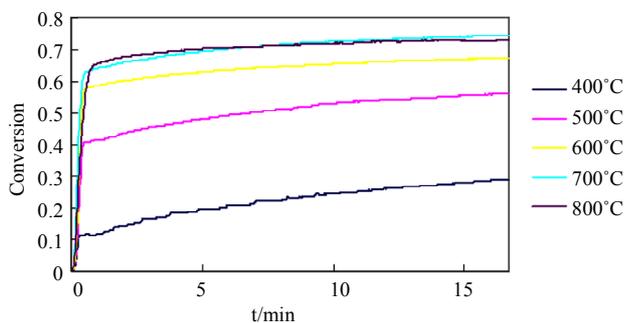

Figure 5. Tube furnace heating system.

Figure 6. Single channel syringe infusion pump and pipe heating system.

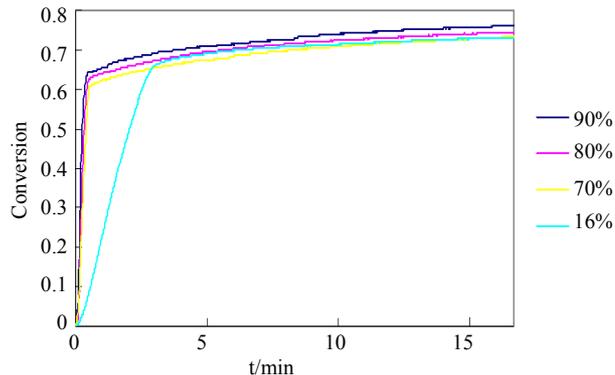**Figure 7. Conversion rate of CaO carbonation at different temperatures.**

As we can see, temperature directly and seriously determines the value of chemical reaction rate constant. In the chemical control stage, the promotion of carbonation conversion rate is 21% from 400°C to 500°C, 32% from 500°C to 600°C, or 18% from 600°C to 700°C. The final conversion rate is 21% higher at 500°C than 400°C, 10% at 600°C than 500°C, or 5% at 700°C than 600°C. So, Temperature is a great influence on the conversion of carbonation, which is because that high temperature will exacerbate the carbonation reaction include chemical reaction rate and final conversion rate. Otherwise, fouling will more likely to occur at high-temperature heating surface, and it should take some appropriate measures to avoiding the unsafe operation of boiler.

4. Effect on Carbonation from CO$_2$ Concentration

In this experiment, each reaction temperature is 700°C, and corresponding CO$_2$ concentration is 16%, 70%, 80%, and 90%. In **Figure 8**, the conversion rate of carbonation include chemical reaction rate and final reaction rate is approximately equivalent in the case of high CO$_2$ concentration such as 70%, 80%, or 90%. For the case of lower 16% CO$_2$ concentration, the chemical reaction rate is slower than that in high concentration CO$_2$ flue, and it needs 190 seconds to go into the production layer diffusion control stage, but it needs only 40 seconds for the case of 80% CO$_2$. Their final conversion rates are almost same, such as 73.14% for 16% CO$_2$, 73.27% for 70% CO$_2$, 74.48% for 80% CO$_2$, and 76.02% for 90% CO$_2$. So, CO$_2$ concentration directly determines the carbonation speed of chemical reaction stage, and its influence on final reaction rate is little.

5. Effect on Carbonation from H$_2$O

Currently it is not a lot about the investigation on any relation with steam and carbonation. In this experimental section, we sprayed water into the stainless steel pipe by a pump, and then water in the tube was rapidly heated into steam. When carbonation reaction, N$_2$ was protective

Figure 8. Conversion rate of CaO carbonation at different concentration of CO$_2$ (700°C).

gas, CO$_2$ concentration was 80%, H$_2$O concentration was 0% - 15%. Experimental results for four temperatures are shown in **Figure 9**. When temperature is 700°C, limestone carbonation conversion rate with 5%, 10%, 15% water is respectively 0.9%, 5.8%, 11.5% higher than that without steam (0% water). At 600°C, the result is almost similar to that at 700°C. When temperature is 400°C, limestone carbonation conversion rate with 5%, 10%, 15% water is respectively 3.1%, 21.5%, 28.6% higher than that without steam. At 500°C, the result is almost similar to that at 400°C. So, steam can facilitate the carbonation reaction of calcined limestone especially at lower temperature conditions.

At the heating surface in the tail of CFB, partly unvulcanized CaO particles will have to continue the carbonation reaction with CO$_2$ and cause fouling and slagging phenomenon. According to above result, steam can increase the intensity and hardness of slag which is more difficult to be removed by soot-blowers, the convective heat transfer coefficient of heating surface will also reduce.

6. Effect on Carbonation from Impurities

In fact, the calcined production of natural limestone is not exactly CaO, also contains SiO$_2$, Fe$_2$O$_3$, Al2O$_3$, MgO and other impurities. Pure CaCO$_3$ and natural limestone are our experimental samples. **Figure 10** is a comparison of two results, CO$_2$ is 80%, and reaction temperatures are 500°C, 600°C, and 700°C. At 700°C, the carbonation conversion rate of CaCO$_3$ reaches 0.65 after 145 seconds, it needs 197 seconds for limestone to reach this rate, and both simultaneously reach 0.67 after 197 seconds. After that time, the carbonation reaction speed of limestone become faster than that of CaCO$_3$, the final conversion rate of CaCO$_3$ is 0.71, and that of limestone is 0.73. The case of 500°C and 600°C is similar to 700°C. We can see from above result that the carbonation reaction speed of pure CaCO$_3$ is faster than that of natural limestone at the chemical reaction stage, and it is reverse at the production
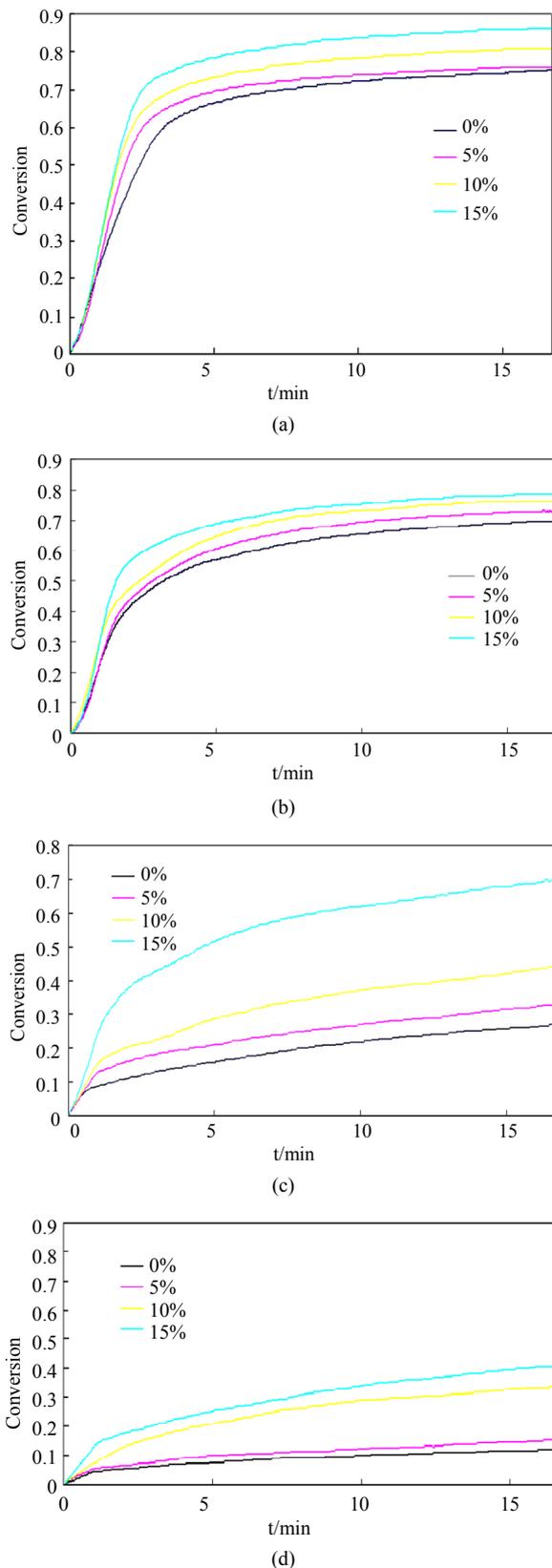
(a)

(b)

(c)

(d)

Figure 9. Conversion rate of CaO carbonation at different concentration of H_2O. (a) 700˚C; (b) 600˚C; (c) 500˚C; (d) 400˚C.

layer diffusion stage. So, the impurities can promote the carbonation reaction speed at the production layer diffusion stage, the reason may be that impurity cause lattice defect in production layer [22].

7. Effect on Carbonation from Cycle Times

The calcinations/carbonation experiment for 10 cycle times was done in this section. Firstly, sample was taken into the furnace, N_2 was protective gas, calcination temperature was 850˚C, insulation time was 10 minutes, the temperature was secondly dropped down to reaction temperature (500˚C, 600˚C, 700˚C), the reaction gas was thirdly switched to 80% CO_2, reaction time was 30 minutes, finally, sample was heated up to 850˚C again. This is a calcinations/carbonation cycle, and cooling/heating speed was 20˚C/min. The experimental result is shown in **Figure 11**.

For this case, carbonation conversion rate is calculated as

$$\alpha_n = \frac{m_n - m_0}{m_0 \cdot A} \cdot \frac{M_{CaO}}{M_{CaCO_3} - M_{CaO}} \tag{5}$$

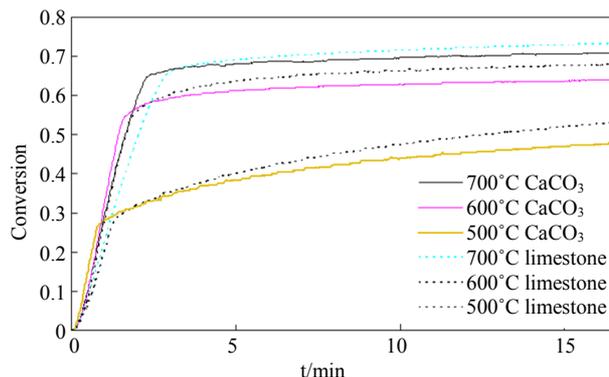In **Figure 11**, we can see that the activity of CaO

Figure 10. Comparison of $CaCO_3$/limestone carbonation reaction.
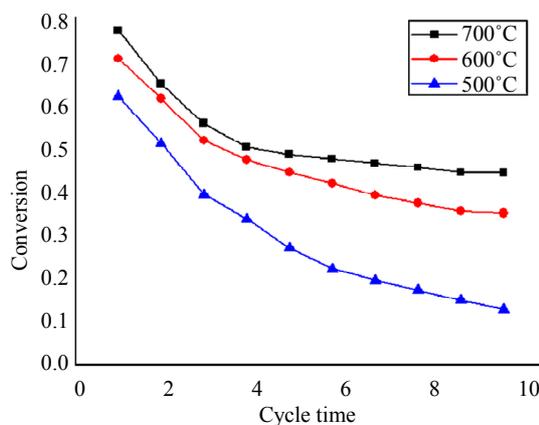

Figure 11. Multiple cycle calcinations/carbonation reaction.

reduces rapidly and the rate decreases by about 30% for the first 5 cycles, and then its curve becomes flat for the next several cycles especially at high temperature. This is mainly due to serious sintering of CaO after multiple cycles. So, in order to maintain a high efficiency, people had to increase the amount of fresh minerals, this will bring a series of problems, such as operating cost, increased wear, pollute. Its mechanism need to be further studied.

8. Effect on Desulfurization from Carbonation

From the above study, we can know that there is a serious problem of carbonation in CFB oxygen-fuel atmosphere. In this section, two experiments were conducted to study the influence on desulfurization from carbonation, one was desulfurization experiment after calcinations, and the other was desulfurization after carbonation. In the first experiment, 10 mg limestone samples were placed into the furnace and heated up to the calcinations reaction temperature (750°C, 800°C, 850°C) by the heating speed of 20°C /min, N$_2$ was the protective gas, hereafter, SO$_2$ (3000 ppm) and O$_2$ were switched in and the desulfurization reaction began, the result of TG curve is shown in **Figure 12**. In the second experiment, 10 mg limestone samples were placed into the furnace, CO$_2$ (80%) was passed into, and then the samples were heated up to the reaction temperature (750°C, 800°C, 850°C) by the heating speed of 20°C/min, finally, SO$_2$ (3000 ppm) were switched in and the desulfurization reaction began, the result of TG curve is shown in **Figure 13**. As we can see, it is a direct desulfurization reaction type in **Figure 13** which is different with that indirect desulfurization in **Figure 12**. Therefore, the carbonation changes the traditional mode of desulfurization.
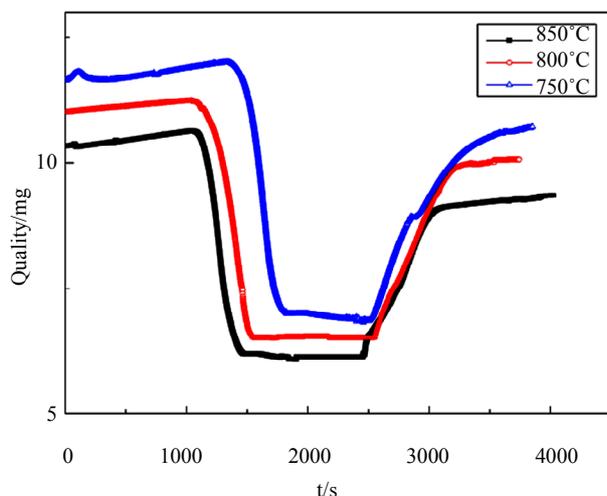
And indirect desulfurization rate is calculated as

Figure 12. Indirect desulfurization TG curve.

$$X = \frac{M_{CaO}}{M_{CaSO_4} - M_{CaO}} \times \frac{\Delta m}{m_0} \qquad (6)$$

Direct desulfurization rate is calculated as

$$X = \frac{M_{CaCO_3}}{M_{CaSO_4} - M_{CaCO_3}} \times \frac{\Delta m}{m_0} \qquad (7)$$

According to above equations, the results of desulfurization rate were calculated in **Figures 14** and **15**. The final conversion rate of direct desulfurization reaction is higher than that of indirect desulfurization, especially at high temperatures. For example, the final rate of indirect desulfurization is <40% at 850°C, but the final rate of direct desulfurization is >60% at this temperature and it is still increasing with time. Obviously, carbonation does not have a negative impact on desulfurization process. **Figure 16** is the micro-morphology of indirect desulfurization particle by scanning electron microscopy (SEM), there is a large number of pores formed after calcination, and they are blocked by desulfurization production and present concave-convex shape. **Figure 17** is the micro-
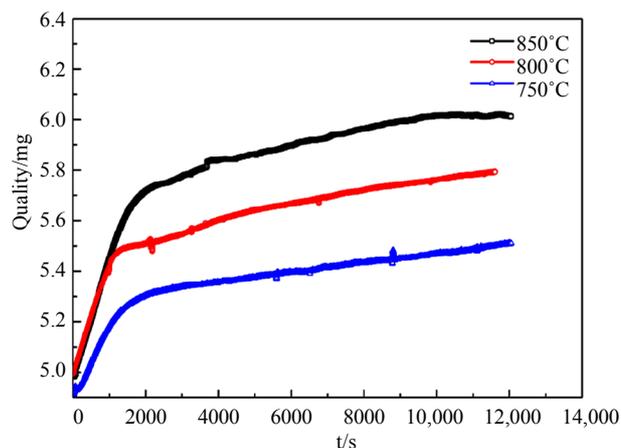
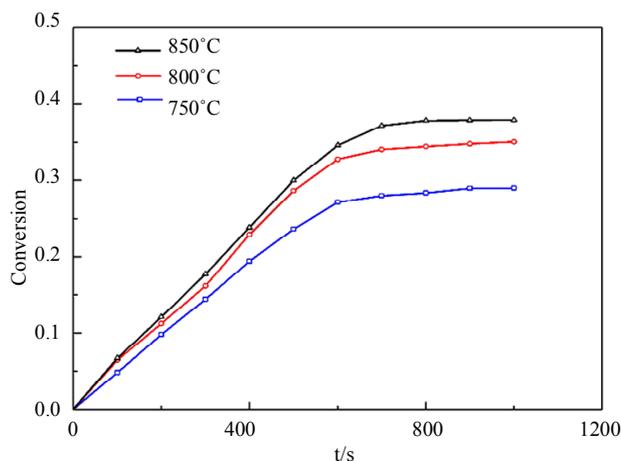**Figure 13. Direct desulfurization TG curve.**
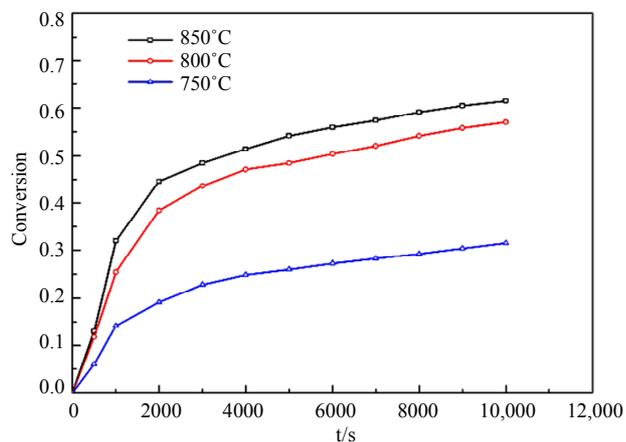
Figure 14. Indirect desulfurization conversion rate.

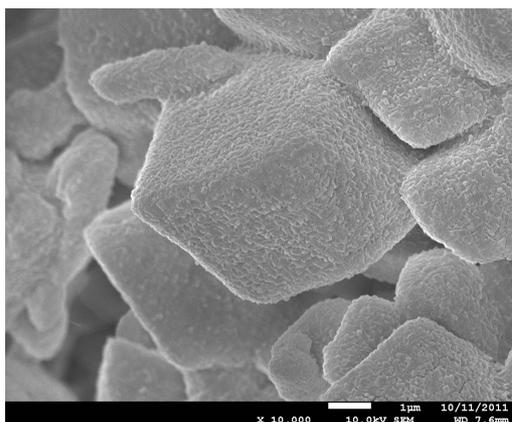**Figure 15. Direct desulfurization conversion rate.**

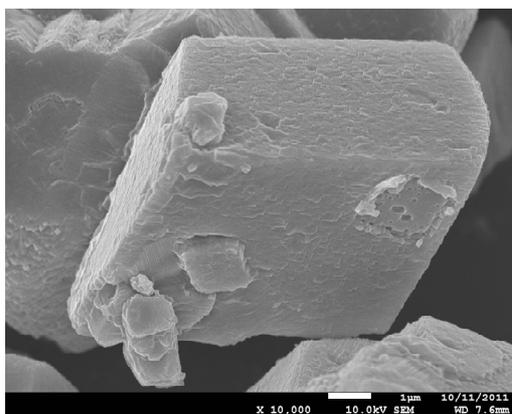**Figure 16. Indirect desulfurization particle surface morphology.**

Figure 17. Direct desulfurization particle surface morphology.

morphology of direct desulfurization particle by SEM, the production layer surface is smooth and dense without any pore. Direct desulfurization can achieve high efficiency without significant pore, which seems to be inconsistent with gas diffusion theory and pore model theory. However, it also shows that solid state ionic diffu-

sion [22] does play a key role which needs a further investigation.

9. Conclusion

The carbonation of calcium-based sorbent is really a serious problem in oxygen-fuel CFB flue gas, and it is closely related to temperature, CO$_2$ concentration, impurities, water vapor, and cycle times. High temperature can promote carbonation process. High concentration of CO$_2$ can inhibit the chemical reaction stage speed of carbonation process, but it has little effect on the final conversion rate. Water vapor can increase the final conversion rate of carbonation. The cycle times will reduce the activity of carbonation. The presence of carbonation changes the traditional boiler flue gas desulfurization chemical model, which is not indirect desulfurization mechanism but direct desulfurization mechanism, and this mechanism will not have a negative impact on SO$_2$ removal efficiency. It should be paid attention that carbonation is easier to damage some flue gas equipments. And, the microscopic mechanism about carbonation and direct desulfurization need deep research in the future.

10. Acknowledgements

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