Study on the influence of the decoking agent on the activity of limestone in wet flue gas desulfurization

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Abstract: Influence of the main components of decoking agent (magnesium nitrate, aluminum nitrate, copper nitrate, ammonium nitrate and actual decoking agent) on the activity of limestone is studied in laboratory by MET method. Results show that magnesium nitrate, ammonium nitrate and copper nitrate almost has no effect on the activity of limestone. With the concentration increasing, aluminum nitrate has an increasing inhibition on the dissolution of limestone. Fly ash has inhibition on dissolution of limestone due to the blockage of limestone pore by fly ash. The actual decoking agent has almost no effect on the limestone.

1. Introduction

Thermal power plants are important power production enterprises in China. The main fuel is coal in thermal power station [1]. The boiler will be influenced by coal quality, combustion condition and other factors. Coal coking phenomenon will occur in the combustion process when low quality coal is burned [2]. Decoking agent can prevent slagging and improve the thermal efficiency of the boiler [3]. As the world's largest coal producing and consuming country, SO$_2$ emissions from coal combustion account for about 85%-90% of the total SO$_2$ emissions in China [4]. Effects of magnesium carbonate, pH value, temperature, particle size on the activity of limestone have been studied systematically [5-7]. However, the effect of the coke removal agent on the activity of limestone has not been reported. The main components of decoking agent are magnesium nitrate, aluminum nitrate, copper nitrate and ammonium nitrate. The effects of these components on the limestone activity will be researched in this article. On the base of above experiments, real decoking agent will be used to study the effect on the activity of limestone.

2. Experiment

2.1. Experimental method

Activity of limestone is measured by MET method. MET method is to measure the relationship between the pH value and the reaction time under the condition of the flow of sulfuric acid. Adding acid, there will be a platform when the pH value reducing. It can be used to compare the reaction activity of different limestone. The desulfurization reaction activity of different limestone can be compared. According to the criteria provided by the United States MET company, the higher the pH retention platform, the better the limestone activity [6]. Experimental device is shown as figure 1.

Limestone samples as 1 grams ($\pm$0.01) CaCO$_3$ alkalinity is weighed and added in a 500ml beaker. 100ml deionized water is added in the same beaker. Then the beaker is placed on a hot plate mixer.
Setting mixing rate 600 rpm and inserting thermometer and pH meter electrode, the beaker is heated to 60$^\circ$C ($\pm$ 1$^\circ$C). The sulfuric acid solution is 0.72mol/l. The titration of calcium carbonate solution is carried out at the rate of 0.75ml/min. Within the first 10 minutes, the slurry pH value is recorded every 2 minutes interval and once every 4 minutes in the next 15 minutes. The slurry pH value should be continuously recorded for 25 minutes. The operating time will be available in 25 minutes to add an excess of acid to the limestone solution to neutralize the equivalent of 1 g CaCO$_3$. Taking the time t as the horizontal coordinate, the pH value is the vertical coordinate, makes the pH-t curve. That is the characteristic curve of the limestone activity.

![Experimental device](image)

**Figure 1.** Experimental device
① Glass tank reactor; ② Digital electric mixer; ③ pH electrode; ④ Digital pH meter; ⑤ Acid burette; ⑥ Thermometer; ⑦ Super thermostatic water bath

**Table 1.** Experimental cases

| Case number | Drugs           | Concentration(mol/l) | Dosage(ml) |
|-------------|-----------------|---------------------|------------|
| Case 1      | ammonium nitrate| 0.1                 | 2          |
| Case 2      | ammonium nitrate| 0.1                 | 5          |
| case3       | ammonium nitrate| 0.1                 | 8          |
| case4       | aluminum nitrate| 0.1                 | 2          |
| case5       | aluminum nitrate| 0.1                 | 5          |
| case6       | aluminum nitrate| 0.1                 | 10         |
| case7       | magnesium nitrate| 0.1                 | 2          |
| case8       | magnesium nitrate| 0.1                 | 6          |
| case9       | magnesium nitrate| 0.1                 | 10         |
| case10      | copper nitrate  | 0.1                 | 4          |
| case11      | copper nitrate  | 0.1                 | 6          |
| case12      | copper nitrate  | 0.1                 | 10         |
| case13      | Decoking agent  | /                   | 5          |
| case14      | Fly ash         | /                   | 0.2g       |
| case15      | Decoking and fly ash | / | 5ml+0.2g |
2.2. Experimental cases
The main components of decoking agent are ammonium nitrate, aluminum nitrate, magnesium nitrate, copper nitrate. Not only effects of single component, but also effects of a certain brand of decoking agent and fly ash on the activity of limestone are carried out in this paper. Experimental cases are shown in table 1.

3. Results and discussion

3.1. Effect of ammonium nitrate
Figure 2 shows the results of case1-3. Dropping 2 ml and 5ml ammonium nitrate solution, the pH value curves coincide with the curve of pure limestone. Stable platform of pH value is approximately 5.5. When dropping 8ml ammonium nitrate solution, the stable platform of pH value slightly decrease and the value is about 5.2. But within 5min-7min, limestone activity curves of different concentrations of ammonium nitrate nearly coincident with that of pure limestone. During the reaction process, three curves are close to overlap. So the effects of ammonium nitrate on limestone activity are not obvious. When ammonium nitrate concentration is high enough, stable pH platform slightly decreases. This cannot explain that ammonium nitrate has a slight adverse effect on the reactivity of limestone. This may be due to the hydrolysis of ammonium ions to produce partial hydrogen ions.

3.2. Effect of aluminum nitrate
Effects of Aluminum nitrate (case 4-6) on the activity of limestone are shown in Figure 3. Dropping 2 ml and 5ml Al(NO₃)₃ solutions, the curve is basically coincident. The pH value of stable platform is slightly lower than the blank. Which shows that low concentration of Al(NO₃)₃ has little influence on limestone activity. But when dropping 10ml Al(NO₃)₃ solutions, pH value of the stable platform decreased to 4.4 and the pH value curve is also below that of pure limestone during the whole process. On the one hand, hydrolysis of aluminum ions to produce hydrogen ions, on the other hand, aluminum hydroxide formed by hydrolysis has flocculation which inhibits the dissolution of limestone particles. So with increasing of Al(NO₃)₃ concentrations, it has more obvious inhibition on limestone dissolution.

3.3. Effect of magnesium nitrate
Results of case7-9 are shown in Figure 4. Compared to the blank, the four curves in the whole process of titration basically coincide, only in the late period of reaction, 14 minutes to the end point of titration, the pH value decreases slightly compared with the blank condition. So we can judge that the magnesium nitrate has no distinct influence on limestone activity and can ignore its effect on wet desulfurization effect.
3.4. Effect of cupric nitrate
Experimental results of case 10-12 are shown in Figure 5. According to Figure 5, adding copper nitrate, pH value drops quickly in first 1-2 minutes and the pH value of stable platform drops from 5.5 to 5.1 compared to the blank. Then each experimental curve basically coincides until the titration end point. Hydrogen ions produced by hydrolysis of copper ions make the pH value of stable platform slightly decreased. Cupric nitrate has little effect on limestone dissolution.

3.5. Effect of the decoking agent
Taking into account the actual production process, the existence of fly ash, the following experiments also consider the impact of fly ash. Comprehensive study of the effect of coke removal agent on limestone activity is carried out. The experimental results of case 13-15 are shown in Figure 6.

From Figure 6 it can be found that with fly ash the pH value of stable platform increases slightly than that of the blank. This is not the dissolution rate of limestone becoming faster, but the fly ash shows alkalescent. In the late reaction, pH value curve of fly ash is below that of the blank sample. The reason maybe the fly ash clogs micro-porous of limestone particles and inhibits the dissolution of limestone. The curve of case 13 coincides with that of case 15. The pH value of stable platform is slightly lower than that of the blank until the end of the titration. This may be due to the hydrolysis of nitrate in decoking agent. There is no obvious evidence that the decoking agent has an inhibitory effect on dissolution of limestone.
4. Conclusions
Effects of decoking agent component on the limestone dissolution are different. Even if the increase of concentration, the effects of ammonium nitrate, nitrate magnesium and cupric nitrate on limestone dissolution are very small; Aluminum nitrate is inhibited to limestone dissolution, and the inhibition becomes more pronounced with the concentration; Fly ash has inhibition to the dissolution of limestone due to blockage of limestone pore by fly ash; Practical decoking agent almost has no inhibition on the dissolution of limestone.

Acknowledgements
Financial supports from the Fund of Nanjing Institute of technology (CKJB201217).

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