Case analysis and preventive measures of limestone-gypsum wet flue gas desulfurization slurry poisoning for 320MW unit

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Abstract. The slurry poisoning of the desulfurization system is a difficult problem in the current desulfurization operation. This paper analyzes the abnormality of the limestone-gypsum wet flue gas desulfurization slurry poisoning of a 320MW unit, and proposes a solution. Through the test method, the slurry composition and gypsum quality analysis was carried out and effective measures were taken according to the actual situation to solve the slurry poisoning phenomenon and ensure the safe operation of the desulfurization system, which is of great significance to the flue gas emission standard of the desulfurization system of the power plant.

1. Introduction  
A 320MW unit of a power plant uses limestone-gypsum wet flue gas desulfurization in its flue gas system. Since the unit was put into operation in 2005, the desulfurization system has been operating stably. However, since the company changed the desulfurization system to a random start in 2012, the pH of the slurry has been on the low side. Professional analysis has determined that the slurry is poisoned and the pH is abnormally lowered. Through operation adjustment and preventive measures, the problem of slurry poisoning was solved and the safe operation of the unit was ensured [1-3].

#2 The unit was started after overhaul. In order to ensure the 100% commissioning rate of the desulfurization system, the desulfurization system was changed from the conventional start-up method to random start-up. The normal start-up method is to start the electrostatic precipitator when the temperature of the electrostatic precipitator reaches 100. After the electrostatic precipitator was put into stable operation, the unit load reached 120MW and put into operation of the desulfurization system, and the random start-up was put into operation of the electric precipitator and desulfurization system before the boiler was ignited. Due to the large change in the operation mode, the abnormal phenomenon of the slurry in the absorption tower occurred after the unit started, and the pH value of the slurry fell to the lowest value of 5.2. Through the conventional method of replenishing the limestone slurry, the pH value of the slurry did not rise, and the operating personnel increased the amount of slurry supplement, at this time, the pH value does not rise but accelerates the decline, and the desulfurization efficiency also has a downward trend. If no effective measures are taken, it will affect the flue gas emission standards. Stop feeding the limestone slurry into the absorption tower. At this time, the pH value has dropped to 4.6, and the slurry density is 1102kg/m³; at 21:35, the pH value drops to 4.0, and a small flow of 1-2t limestone slurry is started. At the same time, the standby oxidation fan is started. After 1h, the amount of limestone slurry was added to 4t/h, and the pH value appeared to rise. After that, 1-2t of limestone
slurry was increased every 30 min, and the maximum was not more than 10 t. During this period, the load and the sulfur content of the desulfurization system inlet did not change significantly; At 2:00 the next day, the pH value 1 returned to 4.86, and the pH value 2 returned to 4.82; at 14:00 on the 20th, the pH value returned to the normal value of 5.2 and the amount of limestone slurry was reduced, and the pH value still rose rapidly; 14: At 15:00, the operation of one oxidation fan was stopped[4, 5].

2. Cause analysis

The water content of gypsum is too large, and the solid content is reduced. Especially the content of gypsum is far below the standard value. The content of limestone in gypsum is nearly 10 times the standard value. A large amount of limestone in the slurry did not participate in the reaction. The slurry density of 1115 kg/m3 displayed when gypsum is produced is not the density after limestone participates in the reaction to form gypsum. In fact, most of the slurry is limestone that has not participated in the reaction.

The start-up method of this unit is random start-up of the desulfurization system. During the random start-up, a large amount of unburned pulverized coal enters the absorption tower and forms a stable compound in the absorption tower slurry, which adheres to the surface of the limestone particles and affects the dissolution reaction of the limestone particles, causing the limestone slurry to be ineffective in adjusting the pH value; resulting in slurry poisoning. At this time, if a large amount of limestone slurry is added, the dissolution of limestone will be further prevented, and the pH value will continue to decrease[6, 7].

During the start-up of the unit, due to the load increase, the sudden change of the flue gas volume will cause the sudden change of the sulfur content of the flue gas entering the absorption tower, causing the reaction in the absorption tower to intensify, the content of CaCO3 decreases, and the pH value decreases. In order to ensure the desulfurization efficiency, the limestone slurry supply must be increased. In order to increase the pH value of the absorption tower, but due to the intensification of the reaction, the calcium sulfite content in the absorption tower slurry greatly increases. If the oxygen content is not increased at this time, the calcium sulfite quickly reacts to CaSO4 • 2H2O (green gypsum), because of CaSO3 • 1/2H2O (calcium sulfite hemihydrate) is highly soluble and first dissolves in water, while CaCO3 dissolves slowly, and forms solid deposits after supersaturation, causing "limestone blind spots".

The density of the slurry in the absorption tower is high and it is not discharged in time. The saturation of CaSO4 • 2H2O in the slurry will inhibit the dissolution reaction of CaCO3.

The quality of the process water is poor, the chloride ion concentration in the system is high, the chloride ion content in the slurry increases, and the chloride inhibits the dissolution of the absorbent.

Poor quality of limestone powder, unqualified particle size passing rate and reduced limestone purity can also cause limestone blind spots in the absorption tower slurry and reduce the reaction effect.

Excessive fluoride ion. The trivalent aluminum in the slurry reacts with fluoride ions to form a complex of aluminum fluoride and other substances, which is in a viscous flocculated state and adheres to the surface of limestone. This will lead to: sealing the surface of limestone particles, preventing them from dissolving, and lowering the pH of the slurry. Chemical tests have also further verified that the slurry does contain a large amount of fluoride ions, which is mainly because coal contains fluoride ions.

The small amount of wastewater discharge will cause the chloride ion in the slurry to exceed the standard, which will affect the reaction effect.

The main phenomena of serous poisoning are:

The pH value of the absorption tower drops abnormally, which is lower than the lower limit of the normal operation control value of 5.2; after the pH value of the absorption tower decreases, the pH value does not rise by increasing the amount of slurry; the slurry density of the absorption tower rises faster than during normal operation; When gypsum, the vacuum belt conveyor is difficult to dehydrate, and the water content of the gypsum is more than 10%; the color of the gypsum is abnormal and black; when the pH value is abnormal, the overflow of the absorption tower is often accompanied by foaming, and...
the foam is black; when the desulfurization efficiency is severe; The sulfite ion in the test slurry is too high; the content of fluoride ion and aluminum ion in the slurry exceeds the standard.

3. Preventive Measures

3.1. Strengthen start-up process monitoring
During the start-up process of the unit, especially when it is started in cold state, powder should be added when the furnace temperature reaches 300° to increase the electric dust removal parameters to minimize the unburned coal powder entering the absorption tower and reduce the pollution of the coal powder to the absorption tower slurry degree. Ensure that the quality of limestone powder is qualified, the purity is above 95%, and the particle size pass rate must meet the pass rate of 95% of the 250 mesh sieve.

3.2. Preventive adjustment
During the normal operation of the unit, it is ensured that the coal quality is up to standard and the concentration of electric dust removal dust does not exceed the standard. During the start-up process of the unit, when the pH value is found to be lowered, it can be added to the absorption tower slurry to add 100kg calcium hydroxide, the addition amount is 10kg/h, and the drainage pit is completely dissolved before being driven into the absorption tower.

3.3. Operation adjustment
When the slurry is found to be poisoned after the unit is started or in operation, and the pH value decreases, the following measures can be taken to restore the pH value to normal to ensure the safe operation of the desulfurization system. Stop adding slurry to the absorption tower. Start the standby oxidation fan when the pH value drops to 4.0. When the pH value drops to 4.0, start a small flow of 1-2kg/m³ of slurry supplement. After that, increase the slurry by 1kg/m³ every 30min and observe the change of pH value. It should rise slowly and make up to no more than 10kg/m³. During this period, the gypsum density reaches 1115kg/m³, and the gypsum production is normal, and the density drops to 1095kg/m³ to stop the plaster production. During the plaster production process, the inspection of the plaster should be strengthened. If the density is low and the plaster is not formed, the plaster can be temporarily stopped. Increase wastewater discharge. Discharge qualified slurry from the absorption tower in normal operation to the absorption tower with abnormal pH value for slurry replacement. Add an appropriate amount of calcium hydroxide and observe the changes in pH. Adjust the parameters of electric dust removal according to coal type, load and ash amount. If the above method is still not effective, carry out the slurry conversion, discharge part of the unqualified slurry, and add fresh slurry.

4. Conclusion
In view of the slurry poisoning phenomenon after the unit is started, the following conclusions are drawn through analysis: during the unit start-up, a large amount of unburned coal powder enters the absorption tower and prevents the reaction of limestone with sulfur dioxide in the flue gas, which is the direct cause of the decrease in pH. When the operators found that the pH value was lowered, increasing the limestone replenishment amount further prevented the dissolution of limestone, which was an indirect cause of the drop in pH value. During operation, if a large amount of dust or heavy metal particles enter the absorption tower due to the poor effect of electric dust removal and the change of coal type, it will also cause slurry poisoning and reduce the pH value of the slurry. Through analyzing the causes of slurry poisoning and taking effective measures, the problem of slurry poisoning was successfully solved and the safe and stable operation of the enterprise's desulfurization system was ensured.

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