Research on countermeasures against slurry foaming and poisoning of desulphurization system in coal-fired power plants

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Abstract. With the completion of the ultra-low emission transformation of coal-fired generating units, the boiler flue gas bypass has been completely cancelled. Under extreme operating conditions of the boiler, the flue gas must pass through the desulfurization system. Excessive dust and unburned fuel in the flue gas enter the desulfurization slurry in large quantities, causing slurry bubbles or even overflow, and indirectly leading to a sharp drop in desulfurization efficiency. The emission concentration exceeds the standard. Based on the analysis of previous research results, the reasons for the foaming and overflow of the desulphurization slurry are summarized. Through theoretical analysis of various causes, the countermeasures against foaming and poisoning of desulphurization slurry were proposed and the feasibility of countermeasures was demonstrated through actual cases. It points out the preventive measures for bubble poisoning of limestone-gypsum wet desulfurization slurry, which has important practical guiding significance for the ultra-low SO₂ emission of the flue gas of the desulfurization system of coal-fired power plants.

1. Introduction
With the completion of the ultra-low emission transformation of coal-fired boilers, the flue gas bypass of the desulfurization tower was completely removed. In the process of cold start of coal-fired boilers and stable combustion with reduced load and oil input, the original flue gas will carry a large amount of oil pollution and excessive smoke directly into the desulfurization tower, causing the slurry in the tower to be poisoned and causing bubbling and overflow. This will not only reduce the desulfurization efficiency and excessive sulfur dioxide emissions, but also threaten the smooth operation of equipment and facilities (such as booster fans, slurry circulating pumps, steel flues, etc.), and seriously affect the safety, environmental protection and stable operation of coal-fired units. [1-2]

2. The hazards of desulphurization slurry foaming and overflow
The limestone slurry in the desulfurization tower produces a large amount of foam. As the foam expands, part of it enters the original flue gas steel flue. After the high-temperature raw flue gas evaporates, the calcium sulfate, calcium carbonate and other substances in the foam expand several times or even ten times the volume and adhere to the inner wall of the flue in large quantities. On the one hand, it will produce peeling stress, destroy the glass flake anti-corrosion layer of the steel flue, and greatly reduce
the service life of the flue; on the other hand, a large amount of calcium sulfate, calcium carbonate, etc. accumulate in the original flue, which will make the original flue effective The cross-sectional area is reduced, the wind resistance of the original flue gas is increased, and the load of the booster fan is increased, which affects the safe operation of the equipment. [3-4]

After the slurry in the desulfurization tower produces a large amount of foam, the half hydrated calcium sulfite in the slurry cannot be oxidized into calcium sulfate dihydrate in time, and the solubility of the half hydrated calcium sulfite is much greater than that of calcium carbonate, which leads to the slurry The medium calcium carbonate is supersaturated and forms a "limestone blank area", and the desulfurization efficiency will drop back rapidly. At the same time, the foam in the slurry continues to increase, and the inlet pressure of each slurry circulation pump is reduced, which not only seriously affects the desulfurization efficiency, but also causes cavitation, which seriously damages the pump body and the impeller. [5-6]

3. Reasons for the foam in the slurry
The foaming substance mixed in the slurry can enhance the mechanical strength, tensile strength and foam stability of the bubble surface film. The main foaming materials are divided into the following two categories.

3.1. Substances in flue gas
A large amount of auxiliary fuel is put into the process of cold start of the boiler or fuel stabilization when the load is reduced, and part of the auxiliary fuel that is not fully burned enters the slurry of the desulfurization tower with the flue gas. The failure of the dust removal system before the desulfurization system caused an abnormal increase in the amount of fly ash entering the desulfurization tower, and the fly ash contained a large amount of inert substances.

3.2. Substances in limestone
Limestone powder often contains a certain amount of magnesium oxide. When its content is low, it can improve the desulfurization efficiency, but when its content reaches a certain concentration, it can react with sulfur dioxide to produce a large amount of foam. These foams wrap calcium carbonate and prevent calcium carbonate. Dissolution and reaction.

4. Countermeasures for slurry foaming poisoning

4.1. Response measures
When there is a large amount of foam overflow at the overflow pipe of the desulfurization tower, the degreasing system should be transported immediately to remove the foaming substances in the poisoned slurry. The filtrate produced by degreasing is not returned to the tower for reuse to reduce the concentration of pollutants such as chloride ions, heavy metal ions, and oil pollution. After the liquid level in the tower is appropriately lowered, the mist eliminator is turned on for flushing, fresh water is added, and the poisoned slurry is cleaned up by the dynamic displacement method. The dynamic displacement method is the most fundamental and thorough method to deal with the foaming of the desulfurization tower, but the disadvantage is that it takes a long time and easily leads to excessive sulfur dioxide emissions. It needs to be used in conjunction with other methods to quickly and effectively eliminate the impact of foam.

4.2. Auxiliary measures
Adding a defoamer into the tower through the drain pit of the desulfurization tower can effectively reduce foam in a short time. A large amount should be added in the early stage. Due to the continuous renewal of the slurry by the dynamic displacement method, the defoamer in the tower will be lost along with the degreasing, and a small amount of replenishment is required in the later stage. However, it
should be noted that the more defoamer is added, the better. Its main component is also organic.
Excessive defoamer can promote the foaming phenomenon.

4.3. Other measures
In order to weaken the foaming strength of the slurry, some slurry circulation pumps and partial oxidation fans can be shut down under the premise of ensuring the ultra-low emission of net flue gas at the outlet of the desulfurization tower to reduce the disturbance of the slurry in the tower and indirectly inhibit the generation of foam.

5. Case analysis
This paper takes the bubbling and overflow of the No. 1 desulfurization system of a thermal power company as an example for analysis. The operating conditions and parameters are as follows: original flue gas sulfur dioxide concentration, 1750 mg/m³, net flue gas sulfur dioxide concentration, 10 mg/m³. Entering the heating period, in order to increase the temperature of the heating pipe network, the No. 1 boiler will be shipped on November 30. On December 6, the temperature dropped sharply. In order to ensure the temperature of the heating network, the No. 2 boiler was shipped from 06:00 to 12:00. During the two boiler departures, a large amount of oil fume entered the No. 1 desulfurization tower (No. 1-3 boilers shared the No. 1 desulfurization system), and the interval between the two boiler departures was short. After No. 1 boiler was shipped, the slurry in No. 1 desulfurization tower did not reach the degreasing density (the degreasing started when the density was higher than 1160kg/m³), and then proceeded to No. 2 boiler and the limestone slurry in the No. 1 desulfurization tower without the oil fume removed. A large amount of oil and some smoke and dust have been collected. At 14:00 on December 6, a large amount of black oil fume foam overflowed from the overflow pipe of the No. 1 desulfurization tower. The preliminary judgment is that the oil fume produced by the two consecutive ignitions caused the limestone slurry of No. 1 desulfurization tower to bubble and poison. At 15:10 on December 6, the online monitoring of sulfur dioxide at the outlet of No. 1 desulfurization system rose rapidly from 3.62 mg/m³ to 61.90 mg/m³. Environmental protection operators immediately added a large amount of limestone slurry to the tower in an attempt to quickly reduce the sulfur dioxide concentration in the flue gas at the outlet of the desulfurization tower. At the same time, a slurry circulation pump was added (5 slurry circulation pumps were running at the same time) and an oxidation fan was added. However, the concentration of sulfur dioxide has not decreased, and there is a tendency to continue to increase.

Immediately after foaming and overflow, the slurry in the tower was chemically analyzed. The analysis result showed that the mass content of calcium carbonate was 8.34%. The calcium carbonate content in the slurry in the desulfurization tower is relatively high. This is mainly because the oil in the slurry can form a protective film on the surface of the calcium carbonate particles to prevent it from dissolving in water. The dynamic balance of calcium carbonate dissolution is broken and the desulfurization efficiency is reduced. The pH value of the slurry will continue to drop, and excess calcium carbonate is suspended in the slurry and cannot react. The content of gypsum crystals is low. This is because the oil on the surface of half-hydrated calcium sulfite cuts off oxygen, which greatly reduces the production of calcium sulfate dihydrate. No amount of air blown can improve the desulfurization efficiency.

At 16:20 on December 6, the following emergency measures were successively taken:
Stop replenishing limestone slurry into the No. 1 desulfurization tower, because calcium carbonate particles are wrapped in oil, and excessive refilling is of little significance to improving the desulfurization efficiency; immediately shutting down two slurry circulation pumps can reduce the generation of foam to a certain extent. One oxidation fan was shut down immediately, because on the one hand, the oxidation fan aggravated the generation of slurry foaming, and on the other hand, excessive oxygen could not increase the oxidation of the oil film of calcium sulfate; the accident slurry pump was turned on and part of the poisoned slurry was discharged inside the accident slurry tank. The liquid level of No. 1 desulfurization tower is reduced from 8.6m to the lowest safe level of 6.2m, which
can effectively prevent foam overflow; after the liquid level is lowered, two sets of degreasing systems are turned on, and the slurry of No. 1 desulfurization tower is degreasing and degreasing filtrate. After being treated by the wastewater treatment system, the discharge reaches the standard, and it is not returned to the tower for recycling. In the process of degreasing, turn on the demister flushing water to add fresh process water to the desulfurization tower; in the process of degreasing, add defoamer into the desulfurization tower, dosing a large amount in the early stage, and replenish a small amount intermittently in the later period; Add NaOH to the desulfurization tower to increase the pH value of the slurry in the tower to improve the desulfurization efficiency. By adopting the above measures, the SO2 concentration of the net flue gas at the outlet of the No. 1 desulfurization system gradually began to decrease, and at 23:20 on December 6th, it fell below 35mg/m³. According to the change of the pH value of the slurry in the tower, start to replenish the limestone slurry, and at the same time add a desulfurization synergist to the tower to enhance the dissolution rate of the limestone powder and improve the desulfurization efficiency.

6. Conclusion
The amount of slurry in the desulfurization tower is large. Once the foaming and overflowing, it will take a long time to completely eliminate it. If the emergency is not appropriate, the daily average SO2 emission may exceed the standard. In the daily operation process, the following preventive measures can be taken to effectively avoid exceeding the standard caused by foaming. Using high-quality limestone powder, strictly control the content of magnesium in the tower stone limestone powder. Properly lower the slurry level in the desulfurization tower before starting the boiler to prevent the slurry from overflowing due to foaming. A proper amount of defoamer can be added preventively into the tower before starting the boiler. Strictly control the amount of fuel used during the start of the boiler to ensure the full combustion of pilot fuel, and prevent large amounts of oil from entering the desulfurization tower from the source. After the boiler has successfully started and ran smoothly, the desulphurization slurry will be de-greased to remove the oily fume in the slurry. A certain amount of NaOH and desulfurization synergist are always available in the factory for emergency needs.

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