Causes and treatments of foaming and overflow of calcium-based wet desulphurization slurry

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Abstract. During the operation of the calcium-based wet desulfurization system, slurry foaming and overflow are prone to occur, which is not conducive to the safe and stable operation of the desulfurization system. In order to solve the problem of slurry foaming, the main properties of the slurry were tested by taking the wet flue gas desulfurization device of a sintering machine of a steel company as an example. The foaming ability of the liquid is characterized by its foaming height and defoaming time, and the influence of surface active substances, particles and metal ions in the slurry on its foaming ability has been studied through multiple experiments. Combining the foaming mechanism and the desulfurization process, the cause of the slurry foaming is analyzed, and measures are given to prevent and treat the slurry foaming overflow to ensure the normal operation of the absorption tower.

1. Introduction
Considering that the calcium-based wet flue gas desulfurization process has the advantages of stable operation, strong operation adjustability, high desulfurization efficiency, and low overall cost, it has become the mainstream process of flue gas desulfurization at home and abroad. By controlling the pH value of the slurry and the amount of oxidizing air aeration, the normal and orderly progress of the entire desulfurization system can be controlled. However, after a large number of desulfurization towers have been running for a period of time, slurry foaming occurs, causing problems such as deterioration of the slurry properties and overflow, which are difficult to eliminate through conventional desulfurization process adjustment. The overflow liquid entering the flue may impact and damage the induced draft fan blades, resulting in dust accumulation in the flue and increasing the resistance of the flue gas. The deterioration of the slurry quality will cause the desulfurization efficiency to decrease and the gypsum quality to fail to meet the standard. Kuang Yanliang analyzed the composition of the foam and believed that process water pollution, unburned organic matter and dust in the flue gas were the reasons for the deterioration of the foaming properties of the slurry. Gu Shengqiu and other Zhi Xing Changcheng et al. attributed the slurry bubble overflow to unburned organic matter, excessive magnesium salts and heavy metals, organic matter in the process water, and dust. Li Xinghua and others can focus on analyzing the influence of process water, flue gas and limestone on slurry bubbling and overflow, and propose corresponding preventive measures for different enterprise situations. [1-2]
At present, there are many reports on the overflow of the absorption tower slurry in the limestone wet desulfurization process due to bubbling, but there are few systematic experimental studies and analyses. Therefore, this paper takes limestone-gypsum wet flue gas desulfurization slurry as the analysis object, and detects the main properties of the slurry. Based on previous research results, a comparative experiment is set up to explore the cause of slurry bubbling and overflow, and corresponding preventions are proposed. And treatment measures. These measures were implemented in the company. Through a return visit to its follow-up operation process, it was found that the slurry foaming overflow was effectively controlled, and the desulfurization system was operating well. [3-4]

2. The mechanism of slurry foaming
Due to mechanical disturbance factors such as bubbling and stirring, the gas with lower density enters the liquid, and the formed bubbles move up to the liquid surface due to buoyancy, forming foam. When the liquid is a pure solvent, the foam quickly loses stability and disappears. Take water as an example. Only when surfactants are added, the surface-active molecules are arranged regularly at the foam gas-liquid interface, so that the foam can exist stably for a period of time. The surface free energy of the gas-liquid two-phase system is the product of the surface tension of the liquid surface and the area of the gas-liquid interface. It is a thermodynamically unstable system. After the foam bursts, the total surface area of the gas and liquid will greatly decrease, and the surface free energy of the system will decrease. Under certain conditions, the foam system is mechanically balanced. Although it can remain stable, once the environment changes slightly, the foam may be unstable and broken. Therefore, the foam system is a pseudo-stable state. [5-7]

During the normal operation of the absorption tower, bubbling of oxidizing air, agitators, and sprayed slurry can cause gas to enter the liquid phase and form foam on the liquid surface. The liquid surface foam is connected to each other in a polyhedron shape. The mutual squeeze of the bubbles and the influence of gravity cause the liquid film to drain to the boundary layer, which makes the liquid film thinner. When the local liquid film thickness is lower than the critical value, the foam is unstable and bursts. At the same time, the pressure of the small foam is high, and the gas in it diffuses into the large foam, the foam continues to expand, and the above drainage occurs again and becomes unstable, and finally bursts. When the viscosity in the foam is relatively large, the viscous force hinders the flow of the liquid in the liquid film and the foam is relatively stable. When there are impurities such as surface active substances in the slurry, the surface tension difference between the surface solution and the inner solution is large, and when the local liquid film becomes thin, the liquid with higher inner surface tension is exposed, forming a tension gradient at the liquid surface. Convection occurs, and the movement of the surrounding liquid with less tension reduces its further thinning. Therefore, the liquid film is strong. Under normal circumstances, limestone enters the desulfurization tower and absorbs sulfur dioxide to form calcium sulfite, which is oxidized to calcium sulfate. When the concentration of calcium sulfate in the slurry reaches a certain level, it is discharged, the slurry is dehydrated to discharge gypsum whose main component is calcium sulfate, and the filtrate enters the absorption tower for reuse. The solid matter in the slurry is mainly calcium sulfate crystals, whose content and pH fluctuate at a suitable level. Because the flue gas contains a small amount of organic matter and salt, it is continuously enriched in the desulfurization tower. When the chloride ion concentration reaches a certain value, the wastewater system starts to operate, reducing the chloride ion concentration in the filtrate and then reuse it. Therefore, the salt and organic matter in the slurry are maintained at a high level. Repair ability and stability, the liquid film can be thinned uniformly instead of partially broken, and the foam can last longer. Explore the cause of slurry foaming and the substances that affect its foaming ability and foam stability, so as to provide technical support and guiding significance for solving the problem of slurry foaming overflow.

3. Experiment and result analysis
This article takes the flue gas limestone-gypsum wet desulfurization device as an example to analyze the causes and influencing factors of the foaming of the desulfurization slurry. The desulfurization
device was completed and put into production on December 25, 2013, with a designed processing capacity of 1000 000 m³/h of flue gas (flue temperature 150°C, system inlet SO2 concentration 1500-2500 mg/Nm³, desulfurization efficiency above 95%, The SO2 emission concentration at the outlet of the desulfurization device is 100 mg/Nm³. After the desulfurization system has operated for a period of time, the phenomenon of bubbling and overflow occurs, which seriously affects the normal operation of the desulfurization process.

3.1. Analysis of slurry properties

After the desulfurization device runs for a period of time, a sample is taken every 3 hours, and the sample is about 300 mL. Put the sampled slurry into 500 mL beakers with 1, 2 and 3 respectively, and let it stand for 2h to observe the change of the slurry. The 3 groups of experimental phenomena are similar: after a period of time, the slurry is divided into 3 layers, the upper layer is about 1/6 of the volume of gray muddy scum, the middle layer is a red water layer that takes up 3/6, and the bottom layer is 2/6. The volume of gray muddy sediment, the upper part of the bottom layer is gray flocculent sediment.

3.2. Experiment and analysis of slurry foaming

Through a self-made simple foaming performance evaluation device, the experiment is completed in a constant temperature room, and it can be considered that the temperature of each group of experimental liquids is the same. Pour 300 mL of experimental liquid into the bubble tube, the height of the liquid layer is about 10 cm, and let it stand for about 10 minutes. Open the industrial nitrogen inlet valve, adjust the gas flow to 100 mL/min, and start timing at the same time, close the inlet valve after 10 minutes and measure the foam layer height. Wait for the foam to disappear and record the time it takes to defoam. Do 3 experiments with the same experimental liquid and take the average of the data. After the experiment of each experimental liquid is completed, clean the bubbling tube and the gas pipeline submerged in the liquid, rinse with distilled water, and then enter the next set of experiments.

In order to explore the performance of the slurry, the following experimental groups are set up: A, the upper scum and middle water layer after standing for 2 hours; B, the filtrate of the slurry filtration; C, calcium sulfate and water are configured into a suspension with a solid content of 10% 500 mL of liquid, add 5g of sodium chloride and 0.5g of magnesium chloride and calcium chloride at the same time; D, calcium sulfate and water are prepared into a suspension with 10% solid content, 500 mL, add 10 g of sodium lauryl sulfate; E, sulfuric acid Calcium and water are prepared into a suspension with a solid content of 10% in 500 mL, 10 g sodium lauryl sulfate is added, and 5 g sodium chloride, 0.5 g magnesium chloride and 0.5 g calcium chloride are added at the same time. Experiments on the above five groups of liquids, the analysis data can be drawn: 1. Without surfactants, the slurry is difficult to generate foam; 2. Metal ions help foam generation, and have little effect on foam elimination; 3. Surface suspended matter helps the formation of foam, and at the same time, it has a significant effect on enhancing the stability of the foam.

4. Possible causes of slurry foaming and overflow

1. During the operation process, due to uneven fuel injection, incomplete combustion, a large amount of organic matter generated enters the absorption tower with the flue gas, and these organic matter generates surface active substances in the slurry.

2. The water quality of the desulfurization supplementary process water did not meet the corresponding requirements, and the addition of surfactant-type bactericides, such as benzalkonium chloride, isothiazolone, etc., caused the slurry to bubble and overflow.

3. The dust collector at the rear of the sintering machine is in poor operating condition, the flue gas dust concentration exceeds the standard, and solid particles containing a large amount of inert substances enter the absorption tower. These tiny solid particles will adhere to the foam surface to form a special hard shell to improve the foam’s performance. The mechanical properties can reduce the drainage of the foam liquid film and at the same time prevent the small foam from combining into a large foam, thereby improving the stability of the foam.
4. The metal ions in the flue gas are continuously enriched in the slurry, which improves the foaming ability of the slurry.

5. The dehydration system of the desulfurization device cannot effectively remove these surface active substances and metal ions that are easily soluble in water, and the waste water system has insufficient processing capacity, resulting in the gradual deterioration of the slurry quality of the absorption tower, and finally the slurry bubbles and overflows.

6. Sudden tripping of the oxidation fan occurred during the operation of the desulfurization system, leading to fluctuations in the liquid level of the overflow pipe. When the design is unreasonable, it will cause a siphon phenomenon and cause a large amount of slurry overflow in the absorption tower.

5. Prevention and treatment measures for slurry foaming and overflow of absorption tower

5.1. Preventive measures
To sort out the causes of slurry foaming and overflow in the absorption tower, to avoid at the source, to deal with and weaken the factors that cause foam formation or enhance the foaming ability of the slurry, and to comprehensively manage a variety of measures to take into account economy and practicability. Reform the fuel combustion system in the sintering process, reduce ignition oil, improve combustion efficiency, and avoid incomplete combustion; control the water quality of the absorption tower, strengthen water quality monitoring and ensure filtration and other pretreatment operations, and control the content of COD and BOD in the water. The parameter index is within the design value range; solve the fault of the dust removal device or even modify the dust removal system to ensure that the concentration of particulate matter entering the desulfurization tower is within 100 mg/m³; control the limestone component within the required range, such as the mass fraction of MgO Control within 2%; control the liquid level of the absorption tower to fluctuate within a reasonable range, and regularly check the level gauge to ensure the correctness of the displayed value of the desulfurization control system; calculate the amount of oxidized air to reduce under the premise of ensuring the oxidation effect The amount of oxidizing air to prevent the remaining air in the slurry from overflowing from the bottom of the oxidation zone to the surface of the slurry in the form of bubbles, resulting in an increase in the slurry foam of the absorption tower; real-time monitoring of the operation status of the absorption tower slurry, wastewater, limestone slurry and desulfurization system, and timely problems Take measures to avoid further foaming and overflow problems.

5.2. Treatment measures
Due to the limitations of actual enterprise conditions, when the above preventive measures cannot be implemented well, the slurry foaming and overflow phenomenon of the absorption tower may occur. Real-time monitoring of the operation of the absorption tower, such as the increase in the outlet pressure of the oxidation fan, the abnormal vibration of the slurry pump, the sudden drop in the flue gas temperature at the inlet of the absorption tower, and the increase in the outlet pressure of the induced draft fan, etc., early detection of bubbling and overflow, and analysis immediately The main reason that may cause foaming and overflow, and take targeted countermeasures to control the situation and prevent the expansion of the accident from affecting the normal operation of the system. On the basis of literature and combined with the conclusions of this experiment, the following measures are provided for reference by enterprises:

Reduce the height of the liquid level. Under the premise of little influence on the oxidation effect, slightly reduce the working liquid level of the slurry to control the occurrence of overflow and prevent the slurry from entering the flue duct of the absorption tower. At the same time, regularly check whether there is liquid flowing out of the drainage pipe at the bottom of the flue in the water seal pit to prevent the slurry from reaching the outlet section of the induced draft fan.

Reduce disturbance. Under the condition that the desulfurization efficiency can be temporarily ignored, a slurry circulation pump is shut down to reduce the disturbance of the slurry inside the absorption tower and reduce the slurry foaming caused by the disturbance.
Increase foam removal. Increase the treatment volume of desulfurization wastewater, reduce the content of metal ions, chloride ions, organic matter, suspended matter and various impurities in the absorption tower slurry, and ensure the quality of the slurry in the absorption tower. Increase the amount of liquid discharged from the oil removal port, remove the surface scum after filtering, and then send it to the wastewater system for treatment.

Sudden external factors such as boiler ignition and fuel injection, temporary process water pollution, etc., cause slurry foaming and overflow in the absorption tower, resulting in low desulfurization efficiency that cannot meet the emission requirements, slurry replacement should be performed. When the situation is not serious, the slurry replacement can be carried out several times to maintain the slurry concentration in the absorption tower to ensure the normal crystallization of gypsum; when the situation is severe, drain all the slurry into the accident slurry tank and re-inject fresh limestone slurry.

Put in defoamer special for desulfurization. Antifoaming agent is the most direct and effective way to remove and inhibit foam, and it is also the most commonly used method for enterprises. However, defoaming agent can only temporarily relieve the problem of slurry foaming in the absorption tower. Once the addition of antifoaming agent is stopped, the absorption tower slurry may be possible. The bubbling overflow phenomenon reappeared. According to the foaming situation of the absorption tower slurry, choose continuous or intermittent addition of special defoamer for desulfurization. If the desulfurization system is only temporarily foamed, a surprise dosing method can also be adopted; if the foaming phenomenon persists, the continuous dosing method should be adopted. The general operation method is that when foaming overflow occurs at the beginning of the absorption tower, the defoaming agent can be added from the pit in a short time in a larger dose, and the foam layer will be thinned quickly in a short time. The foaming and overflow can be controlled within time. Then the added amount can be reduced until it stabilizes at a certain dosage to ensure that the thickness of the foam layer is maintained at a low level for a long time.

6. Conclusion
During the operation of the calcium-based wet desulfurization system, bubbling overflow is one of the more common problems. Experimental results show that surface active substances in the slurry are the main cause of foaming and overflow, and particulate matter and metal ions aggravate this phenomenon. Combined with the desulfurization process, the source of these substances is analyzed, the root cause of the slurry foaming and overflow is given, and the corresponding prevention and treatment measures are given. These measures have been applied in the sintering plant and achieved remarkable results. The desulfurization system has entered a safe and stable operation state.

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