Discussion on the cause of scaling in wet desulfurization system of large coal-fired power plants

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Abstract: The flue gas desulfurization method of large coal-fired power plants is generally limestone/gypsum wet method. But many equipments of this wet desulfurization system during daily operation often cause scaling problems. At present, more literature thinks this scale is caused by the mixing of desulfurized gypsum and fly ash in flue gas. However, this paper analyzes the scale composition and appearance of several power plants in China, which shows that the scale is not a simple mixture of gypsum and fly ash, and is a smelting reaction of fly ash in a complex environment and forms a hard scale of gypsum/limestone-fly ash gel. This kind of scale will endanger the safe and stable operation of the desulfurization system, specific operational and maintenance recommendations are proposed for reference.

1. Foreword
Limestone/gypsum wet flue gas desulfurization (WFGD) is the main method used by coal-fired power plants to control sulfur dioxide emissions from flue gas. It is the preferred desulfurization process for large coal-fired generating units above 300MW. The process has the advantages of mature technology, high efficiency of desulfurization, stable operation, large production of limestone in China, low price, and by-product gypsum is an excellent building material. However, the disadvantage is that due to the complexity of the equipment, there are many problems such as corrosion and scaling of the equipment during long-term operation.

2. Introduction of WFGD flow
The flue gas wet desulfurization facility has the following aspects: preparation system (mainly bucket elevator, limestone silo, ball mill, limestone slurry tank, limestone cyclone station, limestone supply pump), reaction system (mainly absorption tower body, oxidation) Fan, circulation pump, spray layer, defogger, agitator), flue gas system (mainly flue body, baffle door, booster fan, GGH), gypsum dehydration system (mainly gypsum discharge pump, vacuum belt) Machines, gypsum cyclone stations, gypsum warehouses, public systems (mainly process water systems, compressed air systems, etc.), wastewater treatment systems and corresponding electrical systems and thermal control systems. The basic process flow is as follows: the flue gas from the boiler comes out of the dust removal device, passes through the booster fan and GGH, enters the tower from the middle of the absorption tower, and mixes and reacts with the limestone slurry sprayed from the spray layer on the upper part of the absorption tower. Acid gases such as SO2, SO3, HF, and HCl are removed, and the soot that is not removed by the dust
removing device in the flue gas is washed, and the droplets carried in the flue gas are removed while passing through the mist eliminator at the top of the absorption tower. The limestone slurry is prepared in a preparation system, stored in a limestone slurry tank, and sent to the absorption tower through a limestone supply pump. The limestone slurry in the tower is sent to the spray layer through a circulation pump, and the slurry sprayed from the nozzle is formed under a certain pressure. The misty droplets are in gas-liquid contact with the flue gas to form calcium sulfite. The oxidation fan sends air into the slurry tank at the bottom of the absorption tower to further react calcium sulfite to form calcium sulfate (gypsum), and then the gypsum slurry is pumped to the gypsum cyclone station through gypsum transfer for preliminary solid-liquid separation, and then flows to the vacuum belt. The dewatering machine performs vacuum dehydration to make the gypsum water content less than 10%, and then enters the gypsum storage bin and is transported by car. Through the absorption tower, most of the sulfur dioxide of the flue gas is removed. Finally, the treated flue gas is discharged through the chimney.

Figure 1 Process flow chart of wet flue gas desulfurization system

3. Discussion on the cause of scaling

According to the operation of limestone/gypsum wet desulfurization equipment in recent years, the fouling phenomenon of absorption towers, GGH, demisters and other equipment is quite common. The scaling of some coal-fired power plants is very serious, which seriously affects the desulfurization equipment and even the host running safely. The scale of the desulfurization system is morphologically divided into soft scale, crystal scale and hard scale. The soft scale is soft and easy to be washed by water. Most of them are simple accumulation of gypsum, which is easy to appear in the mist eliminator, the bottom of the absorption tower and the flue. The crystal scale is hard, and it is also mixed with powdery substance. There are translucent crystals on the surface and inside, which appear below the surface of the slurry on the inner wall of the absorption tower. It is not easy to appear around the stirrer. Although the crystal scale is hard, the structure is loose and easy to peel off. The hard scale is hard and dense, and cannot be washed away by water. The hard scale is easy to appear on the desulfurization GGH, the absorption tower wall and the tower beam. At present, there are many reports on scaling problems in desulfurization systems. The common view of scaling is the crystallized matter of gypsum and the product of the mixing of gypsum and smoke in the flue gas [1-2].

In the analysis of the hard scale in the desulfurization absorption tower of Maoming Thermal power plant, the main components of the hard scale were found as follows:
Table 1 Hard scale composition of desulfurization system of a thermal power plant (w%)

| Component | Content (hard scale) |
|-----------|----------------------|
| Na$_2$O   | 2.1                  |
| MgO       | 1.1                  |
| Al$_2$O$_3$| 18.2                |
| SiO$_2$   | 31.8                 |
| SO$_3$    | 10.1                 |
| K$_2$O    | 1.7                  |
| CaO       | 14.7                 |
| TiO$_2$   | 1.8                  |
| Fe$_2$O$_3$| 12.8                |

The scale is dense and hard, the compressive strength is large, it is not easy to be broken, and it is easy to block the absorption tower nozzle. See Figure 2 for detail.

Figure 2 a thermal power plant desulfurization absorption tower scale

Through the data of the scale sample, it is found that the main components in the scale sample are smoke, gypsum and the like. The amount of gypsum in the scale sample has a certain amount, it is not the main component, but the content of the main components of the fly ash, Al$_2$O$_3$, SiO$_2$ and Fe$_2$O$_3$, is very high, from the perspective of the hardness and density of the scale, these mixtures are not simply mixed together.

Kang An [3] found that there were new crystals in hard and soft scales when studying the hard and soft scales of Dingzhou Power Plant and Zhangzhou Power Plant. This also indicates that the gypsum and fly ash in the scale are not simply mixed together. In addition, the hard scales of Shaoguan and Huangpu Power Plants are analyzed in Table 3.
Table 2 Dingzhou and Zhangzhou Power Plant Scale composition (w%)

| Component | Dingzhou scale (soft scale) | Quzhou scale (hard scale) |
|-----------|-----------------------------|----------------------------|
| Na₂O      | 1.2                         | 0.9                        |
| MgO       | 3.9                         | 1.3                        |
| Al₂O₃     | 12.7                        | 36.6                       |
| SiO₂      | 23.5                        | 38.5                       |
| SO₃       | 30.9                        | 5.7                        |
| K₂O       | 0.8                         | 0.6                        |
| CaO       | 18.5                        | 6.5                        |
| TiO₂      | 0.8                         | 2.3                        |
| Fe₂O₃     | 6.9                         | 6.8                        |

Table 3 Shaoguan and Huangpu power plant scale composition (w%)

| Component | Shaoguan Power Plant Unit 10 (hard scale) | Shaoguan Power Plant Unit 11 (hard scale) | Huangpu Power Plant (hard scale) |
|-----------|-------------------------------------------|-------------------------------------------|---------------------------------|
| Na₂O      | 2.8                                       | 1.9                                       | 0.6                             |
| MgO       | 1.9                                       | 1.5                                       | 1.0                             |
| Al₂O₃     | 12.2                                      | 14.5                                      | 17.2                            |
| SiO₂      | 37.8                                      | 42.6                                      | 45.2                            |
| SO₃       | 9.1                                       | 8.5                                       | 18.2                            |
| K₂O       | 2.2                                       | 5.0                                       | 0.3                             |
| CaO       | 7.7                                       | 8.2                                       | 10.6                            |
| TiO₂      | 2.1                                       | 1.3                                       | 0.8                             |
| Fe₂O₃     | 12.2                                      | 9.4                                       | 5.4                             |

The scale composition of the wet desulfurization system of five power plants in Table 1 to Table 3, the content of SiO₂, Al₂O₃ and Fe₂O₃ in hard scale is very high, while the content of SO₃ representing gypsum content is relatively small, the highest is 18.2%, the smallest Only 5.7%, the content of SO₃ in the soft scale of Dingzhou Power Plant in Table 2 is as high as 30%, which indicates that the formation of soft scale is mainly due to the existence of a large amount of desulfurization gypsum, which is mainly calcium sulfate dihydrate crystal, gypsum Low strength and poor water resistance [4], when there is a large amount of gypsum in the scale, it is easy to be washed away by water.

Fly ash is dominant in hard scale. In terms of composition, the fly ash belongs to the CaO-SiO₂-Al₂O₃ series, which has potential chemical activity, that is, the fly ash alone does not have hydraulic activity when mixed with water. When the CaO content is high, the fly ash meets water. Can be hardened alone [5], when the CaO content reaches 20%, the pure fly ash is hydrated after adding water to form hydrated calcium silicate, hydrated calcium aluminate or ettringite [5]. The fly ash in the hard scale of the wet desulfurization tower accounts for a large proportion. The main components are SiO₂, CaO·SiO₂·H₂O, Al₂O₃, Fe₂O₃, CaCO₃, etc., and a small amount of Ca(OH)₂[6].

The GGH blockage occurred in Unit 5 of BeiLun Power Plant Phase II. The composition analysis of fly ash and scale samples showed that the content of CaO in fly ash was 5.13%, the fly ash content in hard scale accounted for the majority, and the gypsum content was 9-16% [7].

When the boiler flue gas of a thermal power plant passes through the GGH of the desulfurization system, the absorption tower, etc., the temperature of the flue gas is lowered so that SO₂, SO₃, HCl and HF in the flue gas are condensed on the fly ash, and these acids can re
act with the fly ash. The reaction of H2SO4 with fly ash has the best effect on the conversion of Fe. Under the environment of 50-150°C, there will be crystals on the surface of fly ash. The higher the temperature, the more complex the crystals are, making the fly ash adhere to each other [8]. Even if the mass content of Ca is 0.4%, Ca ions are more likely to be precipitated after treatment with HCl. After the strong acid-treated fly ash, many channels and small number of depressions appear on the surface[9]. The compressive strength of the cement of H2SO4 pretreated fly ash has been significantly improved. The higher the temperature, the higher the compressive strength when the temperature is 30-90°C [10]. In the hard scale of the desulfurization equipment, higher levels of CaSiF6·2H2O, KFe3(SO4)2(OH)6, NaMgAlF6·H2O, Fe2SiO4 and other hydrates were found [11], and when the calcium oxide content was found to be small, it also forms hard scale[12]. Fluoride and sulfate ions are present in the hydrate which indicates that strong acid substances such as HF and SO3 in the flue gas adhere to and react with the fly ash, destroying the fly ash. The vitreous surface of the surface release active substances such as Fe2O3, alkali metal oxides and alkaline earth metal oxides in the fly ash, and hydrates in response to water.

During the process of desulfurization absorption tower slurry, many substances in the flue gas, such as fly ash, are absorbed. These substances are continuously mixed and reacted, so that the surface tension of the slurry becomes smaller and smaller, and the slurry is more likely to adhere to the tower wall of the absorption tower. On the top of the tower beam, etc., the gypsum and fly ash in the slurry are deposited on the tower wall beam and continuously aggregate and aggregate. In the acidic solution, Al2O3 reacts with the acidic substance, and the surface of the fly ash forms a colloid such as Al(OH)3. These colloids have strong flocculation on effect. So that the gypsum and limestone with small particle size in the slurry are adsorbed on the surface of the fly ash to form crystal nuclei and continuously crystallize. In addition, in the acidic environment, the fly ash also undergoes hydration reaction. Under the higher temperature of desulfurization environment (>50°C), the micro-grained gypsum and limestone are filled with voids, so that the fly ash-gypsum system forms a hard and compact gel on the tower wall and the tower beam.

The content of chloride ion in the desulfurization absorption tower is high, which also affects the fouling. 3CaO·Al2O3·CaCl2·10H2O is formed in the fly ash-lime system with CaCl2, and the excitation effect of CaCl2 on low calcium fly ash is better than that. High calcium fly ash is evident [13].

Early studies have suggested that limestone powder is an inert material that is not active and primarily has a filling effect in the gel. However, some studies have suggested that limestone powder not only has a filling effect, but its fineness has a certain influence on the hydration of silicate materials. The finer the fineness, the stronger the effect, and it will react with hydration components to form carbon aluminate. Calcium enhances the early strength of silicate materials[14]. During the desulfurization operation, the limestone powder is continuously added to the slurry of the absorption tower, and the particle size is small, and the average particle size is 40μm, which creates conditions for the scale in the absorption tower, so that the early strength of the scale is enhanced, and it is not easy to be broken. The scale continues to increase.

Limestone/gypsum desulfurization of coal-fired power plants In addition to soft and crystalline scales, there are some hard scales. This is mainly because in the strong acid environment such as H2SO4, HCl, HF in the flue gas, the glass body on the surface of the fly ash under goes structural changes, and the active silicon oxide, alumina, CaO in the fly ash reacts with water, which causes the fly ash to react with various impurities such as gypsum and limestone of fine particle size to form a dense, hard gel which is not easily broken. This kind of hard scaling brings great harm to the operation of the desulfurization equipment. Because the gel accumulates thicker on the tower wall and the tower beam, it will eventually rupture and fall off, and the running agitator collides with the debris. The agitator is damaged, and the debris
is sucked into the slurry circulation pump, colliding with the impeller, causing it to break, and clogging the nozzle of the spray layer, causing the entire spray layer to become clogged and unable to operate.

4. Suggestion

The following measures should be taken for reducing the scaling of limestone/gypsum desulfurization systems in coal-fired power plants:

1. The sulfur content of the coal into the furnace should be reduced. The combustion of high-sulfur coal increases the concentration of sulfur trioxide in the flue gas and reduces the dew point temperature. The fly ash easily reacts with acidic substances.

2. Improve the dust removal efficiency of the dust collector and reduce the dust concentration as much as possible. Since the fine particle size fly ash is not easily caught, and the smaller the particle size, the greater the activity of the fly ash, the fly ash accumulates in the desulfurization absorption tower and deposits on the tower wall and the tower beam to form hard scale.

3. Discharge the desulfurization wastewater in time. The density of fly ash is relatively small compared to gypsum and limestone. After the absorption tower slurry passes through the gypsum cyclone station, all the lighter materials return to the absorption tower. The fly ash will accumulate in the absorption tower, causing the slurry to foam and form a hard dirt. Therefore, the desulfurization wastewater should be discharged in time to discharge the fly ash.

4. Control the concentration of chloride ions in the absorption tower. The high concentration of chloride ions not only causes corrosion of the equipment, but also makes it easier to hydrate the fly ash.

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