Application and performance evaluation of desulfurization wastewater spray drying technology

Zhang Shanshan¹,², Wang Renlei¹, Tang Guorui¹, Dai YU¹

¹Huadian electric power research institute Co., LTD., Hangzhou, 310030

Abstract. In order to realize zero discharge of desulfurization wastewater, spray drying technology of desulfurization wastewater was used in 2x330MW unit of a power plant. Its principle was to use a rotary atomizer for atomization, and a part of hot flue gas was drawn from the SCR denitrification reactor and air preheater into the drying tower, the heat was used to evaporate the desulfurization wastewater in a spray drying tower. The salt in the waste water was mixed with the dust, which was collected and removed by the electric dust remover. Then the water vapor was mixed with the flue gas and finally enters the desulfurization tower. The field test was carried out under the condition that the unit load was 100% and the amount of desulfurization wastewater treated was 5.1m³/h. The results showed that the hot smoke gas volume of drying tower was about 64896m³/h. The smoke temperature at the inlet and outlet of the drying tower were 335°C and 205°C respectively, the moisture content of drying products was only 0.05%. The content of HCl in the flue gas at the inlet and outlet of the drying tower were 55mg/L and 195mg/L respectively, the mass fractions of Cl removal and Cl volatilization in desulfurization wastewater were 87.7% and 12.3% respectively. The increase of Cl content in the dried products had little effect on the utilization of fly ash.

1 The introduction

Limestone-gypsum wet desulfurization process was the most widely used SO₂ removal technology in thermal power industry, it account for about 90% of the capacity of the units that have adopted desulfurization process. Its advantages were mature and reliable technology, high desulfurization efficiency, wide application range and low process cost[1]. The desulfurization wastewater from wet desulfurization is one of the most difficult wastewater to be treated in thermal power plant because of its characteristics of high salt, heavy metal, complex composition, corrosiveness and scaling.

At present, the research and application of zero-emission desulphurization wastewater technology was in its infancy. The zero-emission desulphurization wastewater had been realized in baotou power plant, jurong power plant, yangcheng power plant, etc. The mainstream technology route of these zero-emission desulphurization wastewater projects was "pretreatment + concentration reduction + terminal solidification" [2-5]. If the amount of desulfurization wastewater was small, it could be pretreated and solidified directly. If the amount of desulfurization wastewater was large, pretreatment + concentration reduction could be carried out before solidification treatment. At present, chemical softening + filtration was generally adopted in pretreatment technology, among which chemical softening mainly includes lime-sodium carbonate softening, lime-flue gas softening, naoh-sodium carbonate softening, etc.

Filtration includes tube microfiltration, ultrafiltration, nanofiltration, etc[5-7]. Concentration reduction technologies mainly included membrane concentration and thermal concentration, among which membrane concentration technologies mainly include nanofiltration membrane, positive osmosis membrane, reverse osmosis membrane and electrodialysis membrane [8-10], while thermal concentration technologies mainly include multi-effect evaporation, steam recompression evaporation and low-temperature flue gas waste heat evaporation[11-12]. At the end of solidification technology mainly include evaporation pond, evaporation crystallization technology and flue gas vaporization drying technology[13-18], which was divided into multiple effect evaporation and crystallization technology evaporation crystallization process (MED) and steam compression (MVR/TVR) evaporation crystallization process, dry flue gas vaporization technology was the main flue gas vaporization drying technology and the bypass flue gas vaporization drying technology, which was divided into two-fluid atomization technology, mechanical rotary atomizing technology, fluidized bed drying technology and so on.

2 Application of zero emission technology of desulfurization wastewater spray drying
2.1 The technology principle

Zero discharge spray drying technology of desulfurization wastewater was one of by-pass flue gas evaporation drying technology. Its principle was to use a rotary atomizer for atomization, and a part of hot flue gas was drawn from the SCR denitrification reactor and air preheater into the drying tower, the heat was used to evaporate the desulfurization wastewater in a spray drying tower. The salt in the waste water was mixed with the dust, which was collected and removed by the electric dust remover. Then the water vapor was mixed with the flue gas and finally enters the desulfurization tower. Thus the zero discharge treatment of desulfurization wastewater was completed.

2.2 Overview of engineering applications

The 330MW coal-fired power unit of a power plant adopts the limestone-gypsum wet desulfurization technology. In the actual operation process, a certain amount of desulfurization wastewater was generated. The power plant chooses the desulfurization wastewater spray drying technology for zero-emission treatment. According to the transformation technical agreement and related requirements, under the condition of designed coal, when the boiler was 100% loaded, the designed treatment capacity of the drying tower was 5m$^3$/h, and the dry slag moisture content at the bottom of the drying tower was less than 0.2%. The relevant performance guarantee values were shown in table 1.

| Item                          | Guarantee value |
|-------------------------------|-----------------|
| Design wastewater treatment volume | 5m$^3$/h       |
| Moisture content of drying products | ≤0.2%          |
| Boiler efficiency influence value | ≤0.5%          |
| Drying tower outlet smoke temperature | ≤180°C         |

3 Evaluation of zero emission technology of desulfurization wastewater spray drying

During the test, several parallel samples of desulfurization wastewater were taken from the waste water tank every day, and the water quality of the sampled wastewater was tested. The amount of desulfurization wastewater at the entrance of drying tower was measured by fortalow-s10c1-00c ultrasonic flowmeter in Japan. The test results of water quality and water volume of desulfurization wastewater were shown in table 2.

| Water quality of the project | Unit     | Data  |
|-----------------------------|----------|-------|
| Soluble solid               | mg/L     | 41400 |
| Suspended solids            | mg/L     | 7850  |
| Cl                           | mg/L     | 14500 |
| pH                          | /        | 7.97  |
| On-site test of desulfurization wastewater | m$^3$/h | 5.1   |
| Online desulfurization wastewater volume | m$^3$/h | 5.0   |

It could be seen from table 2, the dissolved solid content of desulfurization wastewater was 41400mg/L, the Cl content was 14500mg/L, the on-site test of desulfurization wastewater was 5.1m$^3$/h, and the flow error with the online instrument was 2%, indicating that the electromagnetic flowmeter of desulfurization wastewater at the entrance of the drying tower was accurate, and the amount of desulfurization wastewater injected into the drying tower was 5.1m$^3$/h, which meet the test requirements.

3.2 Moisture content of drying products

During the test, ash samples were collected at the bottom of the dry tower twice a day, about 100g each time. The collected slag samples were weighed in the beaker respectively, and then put into the oven to dry together until constant weight, and then put into the dryer to cool to room temperature and weigh. According to the weight change of slag samples before and after drying, the moisture content of the dry products at the bottom of the drying tower was calculated to be about 0.05%, which met the requirements of the technical agreement (≤0.2%).

3.3 The temperature change of drying tower

During the test, the flue gas temperature at the inlet and outlet of the drying tower was tested respectively. The temperature curves of the inlet and outlet of the drying tower were shown in figure 1.

3.1 Water quality and quantity of desulfurization wastewater
It could be seen from figure 1, drying tower entrance smoke temperature maintained at about 335 °C, the high temperature flue gas in the tower of dry desulfurization wastewater for atomization evaporation, drying tower outlet smoke temperature down to about 205 °C, drying tower inlet and outlet flue gas temperature was 130 °C, drying tower outlet smoke temperature significantly higher than the technical agreement requirements (outlet flue gas temperature ≤ 180 °C), description of drying tower was introduced into hot smoke volume may be larger.

3.4 Influence on boiler efficiency

The desulfurization wastewater spray drying technology USES the newly built drying tower in the bypass to conduct atomization and evaporation of desulfurization wastewater in the drying tower after extracting the high-temperature flue gas from the denitrification unit and in front of the air preheater. After extracting a certain amount of high-temperature flue gas, the amount of high-temperature flue gas entering the air preheater was reduced to some extent. On the premise that the heat exchange efficiency of the air preheater remains unchanged, the amount of heat obtained by the primary air and the secondary air through the air preheater was reduced, which had a certain impact on the efficiency of the boiler. During the test, parameters such as hot exhaust gas volume, total exhaust gas volume of the boiler, inlet and outlet smoke temperature of the air preheater were tested. Table 3 was the influence table of desulfurization wastewater atomization drying technology on the air preheater during the test.

Table 3. Effect of spray drying technology on air preheater for desulfurization wastewater

| Item                        | Unit   | Data |
|-----------------------------|--------|------|
| Desulfurization wastewater  | m³/h   | 5    |
| Draw hot smoke volume       | m³/h   | 64896|
| Total smoke gas             | m³/h   | 998760|
| The percentage of the total amount of smoke | %      | 6.5   |
| Dry tower entrance smoke temperature | °C    | 335   |
| Drying tower outlet smoke temperature | °C | 205   |
| Air preheater inlet smoke temperature | °C | 335   |

It could be seen from table 3, the average amount of hot smoke gas extracted from the drying tower was about 64896m³/h, accounting for 6.5% of the total flue gas of the boiler. According to the calculation, the overall efficiency of the boiler decreased by 5.5%, slightly exceeding the design value (5%). Combined with figure 2, it could be judged that the amount of hot smoke was relatively large, resulting in higher smoke temperature at the outlet of the drying tower, which had a certain impact on the boiler efficiency.

3.5 Chlorine balance of drying tower

The chlorine balance in the drying tower was shown in figure 2. The content of chlorine in the drying tower was calculated in 1 hour, as shown in table 4.

Table 4. The content of chlorine in drying tower

| Item                        | Flow rate/concentration | Cl content | The total Cl |
|-----------------------------|-------------------------|------------|--------------|
| The desulfurization wastewater | 5.1m³/h                   | 14500mg/L   | 74.0kg/h     |
| Smoke from the entrance of the drying tower | 64896m³/h               | 55mg/m³     | 3.6kg/h      |
| Dust at the entrance of the drying tower | 24g/m³                   | 0.12%       | 1.9kg/h      |
| Flue gas from drying tower outlet | 64975m³/h               | 195mg/m³    | 12.7kg/h     |
| Dust at the outlet of the drying tower | 30g/m³                   | 3.23%       | 63.0kg/h     |
| Dry ash at lower end of tower | 1.7g/m³                 | 3.22%       | 3.6kg/h      |

It could be seen from figure 2 and table 4, the main sources of chlorine in the drying tower include chlorine in the desulfurization wastewater, HCl in the flue gas at the inlet of the drying tower and chlorine in the dust at the inlet of the drying tower, among which the chlorine content in the desulfurization wastewater was the main one. The effluent of chlorine from the drying tower mainly includes HCl in the flue gas at the outlet of the drying tower, chlorine in the dust at the outlet of the
drying tower and chlorine in the low slag of the drying tower. The total chlorine content at the inlet and outlet of the drying tower were 79.5kg/h and 79.3kg/h respectively, and the chlorine content in the drying tower was basically balanced.

3.6 Chlorine removal and volatilization of desulfurization wastewater

After the desulfurization wastewater was atomized and dried by the drying tower, most of Cl was collected and removed by the electric dust remover, and a small part of Cl volatilization return to the absorption tower with the flue gas. As can be seen from table 4, the content of gaseous Cl in the flue gas at the inlet of the drying tower was 55mg/m³, and the content of gaseous Cl in the outlet flue gas was 195mg/m³, an increase of 140mg/m³, mainly due to the increase of HCl content in the outlet flue gas caused by chlorine volatilization of desulfurization wastewater. According to the calculation, the mass fraction of chlorine removal from desulfurization wastewater was 87.7%, and the mass fraction of Cl volatilization was about 12.3%, indicating that 12.3% Cl in desulfurization wastewater returns to the desulfurization tower. When the amount of desulfurization wastewater remains unchanged, the concentration of chlorine ions in the desulfurization tower would increase. In the actual operation process, the desulfurization wastewater was discharged continuously and the volume flow of the desulfurization wastewater increases, which would maintain the Cl concentration in the desulfurization tower within a certain reasonable range.

3.7 Effect on fly ash

After atomization and evaporation of desulfurization wastewater through drying tower, most Cl was removed by mixing with dust. According to the one-hour plan, Cl in desulfurization wastewater mixed with dust was 64.9kg/h, and the total content of Cl in fly ash was 66.6kg/h, while the amount of fly ash produced by one boiler was 24.0t/h, and the proportion of Cl in fly ash was 0.28%. According to the mixing ratio design principle of fly ash concrete, if fly ash was incorporated into cement at 20%, the content of Cl in cement was 0.056%, which meet the requirements of gb175-2007 "general Portland cement" of 0.06%[19]. Therefore, bypass flue evaporation had little effect on the recycling utilization of fly ash.

4 Conclusion

Experimental results showed that:
(1) The smoke temperature at the inlet and outlet of the drying tower were 335°C and 205°C, the outlet smoke temperature of drying tower were obviously higher than the requirements of technical agreement (outlet smoke temperature ≤ 180°C). The overall efficiency of the boiler decreased by 5.5%, which exceeded the design value (5%). It could be judged that the amount of hot smoke was too large, resulting in a higher smoke temperature at the outlet of the drying tower, which had a certain impact on the boiler efficiency. The moisture content of drying products at the bottom of drying tower was about 0.05%.
(2) The content of chlorine in drying tower was basically balanced, the total chlorine content at the inlet and outlet of the drying tower were 79.5kg/h and 79.3kg/h, the main sources of chlorine were chlorine in desulfurization wastewater, HCl in flue gas and chlorine in dust at the inlet of the drying tower. The main effluents of chlorine were HCl in flue gas, chlorine in dust and chlorine in low slag. The increase of Cl element in fly ash was 64.9kg/h, which had little impact on the resource utilization of fly ash.
(3) The removal mass fraction of Cl in desulfurization wastewater was about 87.7%, the mass fraction of Cl volatilization was 12.3%. Chlorine volatilization of desulfurization wastewater results in the increase of HCl content in export flue gas, which would increase the amount of desulfurization wastewater and the amount of added water in the process.
(4) After the desulfurization wastewater was atomized and evaporated by the by-pass drying tower, the salt in the waste water was collected and removed along with the dust, and the evaporated water vapor entered the desulfurization tower along with the flue gas. After the desulfurization tower condenses, the desulfurization process water was indirectly supplemented, so as to realize zero discharge of desulfurization wastewater.

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