Flue Gas Treatment of Desulphurization Wastewater

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Abstract. Desulfurization wastewater from thermal power plants has high salinity, strong corrosiveness and great harm to the environment, which is the key and difficult point to realize zero discharge of wastewater. The conventional evaporative crystallization process is complicated with many equipments and high investment cost and operation cost. Based on the problems of the traditional evaporation crystallization process, the field of zero discharge of desulphurization wastewater is more inclined to flue gas treatment. In this paper, the flue gas evaporation technology is introduced and analyzed, and various processes and combinations are analyzed and compared, as well as the cost comparison. Finally, it is confirmed that spray drying evaporation technology has the most market potential.

1. Preface

1.1. Thermal power industry market overview

Due to the natural conditions of "rich coal, little gas and short of oil", China's energy structure is dominated by coal, while the power generation industry is also dominated by thermal power generation, supplemented by hydropower, wind energy, nuclear energy, solar energy and other power generation energy. In recent years, although the generating capacity and newly installed capacity of thermal power generation in China have declined somewhat, thermal power generation is still the most important way of power generation in China.

According to the “National power supply and demand situation analysis forecast report in 2019-2020 statistics of China Electricity Council"(hereinafter referred to as the" report ") show that the country consume 7.23 trillion kilowatt-hours of electricity in 2019, year-on-year growth 4.5%, the electricity consumption of the tertiary industry and residents of urban and rural accounts for 51% of the growth rate of electricity consumption. National installed power-generating capacity is 2.01 billion kw, including 840 million kw from non-fossil energy, up 5.8 percent year-on-year, accounting for 41.9 percent of the total installed capacity, up 1.1 percentage points from the end of last year[1].

To sum up, in 2019, China's power supply and demand continued of easing in the near future. According to the report of China Electricity Council, it is estimated that the electricity consumption of the whole society will continue to grow steadily in 2020. Without the influence of large-scale extreme temperature, the electricity consumption of the whole society will increase by 4%-5% compared with that of 2019.By the end of 2020, China's installed power generation capacity is expected to reach 2.13 billion kw, up by around 6%[1].
1.2. Flue gas treatment technology for desulphurization wastewater
At present, the traditional chemical treatment methods of neutralization, precipitation, flocculation, concentration and clarification are often used in the waste water after wet flue gas desulfurization in thermal power plants, but the chloride ion in the water still cannot be removed. Because of the corrosive effect of high concentration of chloride ion on the system, the treated wastewater cannot be recycled into the system, and the sludge generated needs to be treated separately[2].

Conventional desulfurization wastewater treatment technologies include the use of desulfurization wastewater in coal yard spray or wet slag discharge systems. And "pretreatment + evaporation concentration + crystallization" technology as the representative of the desulfurization wastewater zero discharge technology is also widely used technology. However, the traditional desulfurization wastewater treatment process system is complex, with a large number of equipment, poor working environment, high investment and operating costs, and cannot remove Cl\(^-\) from the wastewater[3].

Flue gas from the rear end of the boiler contains a lot of waste heat, if this part of the flue gas is used to spray evaporation on the desulfurization wastewater. In the waste water, fine solid particles of micron scale are suspended in the flue gas together with dust, and are collected and discharged with the flue gas into the electrostatic precipitator, and the waste water vapor is discharged with the flue gas. This method can not only realize the zero discharge of desulfurization wastewater and meet the practical requirements of environmental protection, but also greatly reduce the amount of chemicals used in chemical treatment methods, which has important engineering practical value. The flue gas evaporation technology realizes the energy recycling, saves energy, reduces the energy consumption cost of desulfurization wastewater treatment, and conforms to the national strategic requirements of energy conservation and emission reduction.

2. Introduction of flue gas evaporation technology

2.1. Main flue gas evaporation technology

2.1.1. Techniques and Principles. Flue gas vaporization technology of desulfurization waste water is to use gas-liquid two-phase flow nozzle to atomize desulfurization waste water and spray it into the flue gas between the air pre-heater and the dust collector, as shown in figure 2. The waste water is completely evaporated by using the waste heat of flue gas, so that the pollutants in the waste water are transformed into crystals or salts and collected by the dust collector together with the fly ash[4]. The technological process is shown in figure 1.

Figure 1. Flue gas evaporation technology.
Figure 2. Atomize and mix.

The simple process flow of flue gas evaporation technology for desulfurization wastewater is shown in figure 3. High pressure pump and atomizing nozzle are important equipment in the system. The control of droplet size after atomization is the key to the success of the process[5].

Figure 3. The simple process flow of flue gas evaporation technology.

2.1.2. The main problem with this technology. Ash accumulated in the flue. The change of boiler load, improper arrangement of the nozzle and wear and blockage of the nozzle may cause ash accumulation in the flue.

The nozzle is worn and blocked during operation.

A small amount of coarse droplets may enter the subsequent esp, resulting in wall adhesion and corrosion[6].

2.2. By-pass flue gas evaporation technology
The main flue technology may increase the risk of safe and stable operation of boiler system, therefore, the main flue gas technology was optimized and improved, and the by-pass flue gas evaporation technology was introduced.

2.2.1. Techniques and Principles. The inlet of the by-pass evaporation system is located behind the selective catalytic reduction system (SCR) and in the front flue of the air preheater, while the outlet is located behind the air preheater and in the front flue of the dust collector. The entrance and exit of the bypass flue are separated from the main flue by the electric isolation baffle to ensure the stable operation of the power plant. The entrance of the bypass flue is equipped with an electric regulating baffle to regulate the flow and velocity of flue gas and ensure the efficient evaporation of droplet[7]. The technological process is shown in the figure 4.
Figure 4. By-pass flue gas evaporation technology.

The flue gas temperature at the entrance of the bypass flue is basically maintained at about 330℃. After rapid mass transfer and heat transfer between the atomized droplets of concentrated water and the high-temperature flue gas, the temperature in the middle section drops to about 270℃. The flue gas temperature at the outlet of the bypass flue duct is basically maintained at about 135℃, which is basically consistent with the flue gas temperature at the outlet of the air preheater. The gas pressure and liquid pressure of the atomizing device in the bypass flue are around 0.5mpa. Under this condition of the gas-liquid ratio, the diameter of the atomized droplet is within 100μm, which has a large specific surface area and ensures the efficient evaporation of the droplet.

2.2.2. The characteristics of the by-pass evaporation technology. The advantages of by-pass evaporation technology are as follows: small floor area and low project investment; High degree of automation, easy operation improve the operation and maintenance level of the system; The isolation plate is installed at the inlet and outlet of the bypass flue, which can be isolated from the main body of the power plant without affecting the daily operation of the power plant.

However, the by-pass evaporation technology requires chemical pretreatment before desulphurization waste water enters the flue gas for evaporation, and the waste water is concentrated and reduced by the double membrane method, which increases the complexity of the system and the investment cost and operation cost of the system.

2.3. Spray drying tower evaporation technology

2.3.1. Techniques and Principles. The desulphurization wastewater after pretreatment and concentration reduction is atomized into fine droplets with particle sizes of about 10~60μm by the rotating atomizer, and then sprayed into the drying tower. The boiler hot flue gas in front of the air preprocessor is used as a heat source to enter the drying tower to evaporate the wastewater. The moisture enters the flue gas, after the salt in the waste water is dried, part of it falls into the bottom of the drying tower and is collected and transferred, and the rest of the drying products enter the dust collector for treatment with the flue gas, so as to achieve the goal of zero discharge of desulfurized waste water[8]. The technological process is shown in the figure 5.
Compared with main flue evaporation and bypass flue evaporation, spray drying evaporation technology requires an evaporation tower, which increases equipment investment, floor space and power consumption. However, this process is more capable of ensuring that all droplets in the flue gas evaporate before entering the dust collector. Compared with evaporative crystallization technology, spray drying technology has simple equipment, simple process and low energy consumption. Of course, when the air is pumped from the front end of the air preheater, whether it will have a certain impact on the thermal efficiency of the boiler, whether it will have an impact on the dust collector, as well as the effects of flue structure, wastewater quality and atomized particle size of nozzle on evaporation efficiency need to be demonstrated through a large number of simulations, experiments and actual operating conditions[9].

2.3.2. The characteristics of the spray drying tower evaporation technology. The spray drying evaporation technology adopts the rotary atomizer, which has a wide range of spray quantity adjustment compared with the dual-fluid atomizing nozzle. It is highly adaptable to the change of working conditions, is not easy to block, and operates stably and reliably, without the risk of affecting the main system. Through the comparative analysis of evaporative crystallization technology, flue gas evaporation technology and spray drying evaporation technology, Mitsubishi Heavy Industries believes that spray drying technology has the most competitive market. However, the disadvantage of this technology is that the boiler thermal efficiency decreases by about 0.30~0.50%.

2.3.3. Effect of desulphurization wastewater evaporation on electrostatic precipitator. The evaporation of desulphurization wastewater will increase the humidity of flue gas and reduce the flue gas temperature to a certain extent, but the flue gas temperature is still higher than the acid dew point temperature, which will not cause corrosion of the flue and ESP. The increase of the humidity of the flue gas and the decrease of the temperature increase the specific resistance of the dust, which is conducive to the dust removal effect of the electrostatic precipitator and improves the dust removal efficiency to a certain extent. After the desulfurization wastewater evaporates, the driving speed of flue gas and the humidifying effect of flue gas are both conducive to the increase of dust particle size, the capture of electrostatic precipitator and the efficiency of dust removal. The desulfurization efficiency increases with the decrease of the inlet flue gas temperature, and the dust removal efficiency also increases with the increase of flue gas humidity, so that the content of the flue gas flying ash into the desulfurization tower is reduced and the problem of blocking and scaling of the defogger is alleviated[10].

2.3.4. Effect of desulphurization wastewater evaporation on desulphurization process. Some impurities from the evaporated wastewater will enter the desulfurization system with the flue gas, which will increase the concentration of dust particles to a certain extent, which will have adverse effects on gypsum crystallization. The decrease of flue gas temperature is beneficial to the
crystallization of gypsum, and the decrease of flue gas temperature improves the desulfurization efficiency, and the content of calcium sulfate in the desulfurization slurry also increases[11].

2.3.5. Effect of desulphurization wastewater evaporation on comprehensive utilization of fly ash. The accumulation density of fly ash is calculated by 0.76t/m3, and the fly ash content of a single unit is 45.6t/h. The amount of chloride ion captured by the dust collector is 0.14t/h after the desulphurization wastewater is all evaporated through the flue. The proportion of chloride ion in total ash content is 0.3%.

When fly ash is used as raw material for cement, according to article 5.1 of GB175-2007 "General Portland Cement", the proportion of fly ash in Portland cement is 20%~40%. Therefore, after the fly ash is used for cement production, the content of chloride ion in cement is 0.06%~0.12%. According to article 7.1 of GB175-2007 "General Portland cement", chloride ion (mass fraction) in cement ≤0.06%. Therefore, after desulfurization wastewater evaporates through the flue, the mixing ratio of fly ash in cement should not be higher than 20%.

When fly ash is used to accompany concrete, according to article 4.1 of GB/T1596-2005 "Fly ash used in Cement and Concrete", the chloride ion content of fly ash is not required[12].

2.3.6. Effect of desulphurization wastewater evaporation on boiler thermal efficiency. Spray drying of desulfurization wastewater requires hot flue gas from the inlet of air preheater, which will affect boiler efficiency. Generally, the flue gas discharge is ideally controlled between 3-5%, the hot air temperature decreases by 4-6℃, and the boiler thermal efficiency decreases by about 0.30-0.50%[13].

2.3.7. The key point of spray drying tower evaporation technology. Atomization technology: The key of atomizing technology is to choose a more professional rotary atomizing nozzle, which is more suitable for desulfurization waste water properties. It should have the advantages of high reliability, easy maintenance, wear resistance, uniform atomization and so on. Secondly, its spray quantity has a wide range of adjustment, strong adaptability to changes in flue gas temperature, flue gas composition, and flue gas quantity, etc., and it can quickly respond to changes in working conditions of the unit.

Mixing technology of flue gas and droplet: A professional rotating atomizer suitable for desulfurization wastewater is adopted to ensure the fineness and evenness of fog drops. The flue gas distributor matched with the nozzle divides the incoming hot flue gas into two parts, DC gas and cyclone gas, to ensure that it is fully mixed with the droplet under the minimum amount of flue gas, so as to realize rapid evaporation and penetration and avoid the occurrence of "wall sticking" phenomenon[14].

3. Process comparison and cost accounting

3.1. Flue gas evaporation process route

3.1.1. Single pretreatment + Spray drying evaporation. Application scope:

Desulphurization wastewater quantity per 100MW unit is ≤ 1.0t/h, without reduction.

Features: Simple process, low investment and operation cost. To upgrade or expand the power plant, the existing three-box process can be used to upgrade, to make the pretreatment effluent meet the inlet water quality requirements of the drying tower.

3.1.2. Pretreatment + Concentration reduction + Spray drying evaporation. Applicable Scope:

1.0 t/h < the desulphurization wastewater quantity per 100MW unit is ≤ 2.0 t/h. The salt content is concentrated to 5%-8% by the membrane reduction method of "UF/MF + RO".

2.0 t/h < the desulphurization wastewater quantity per 100MW unit is ≤ 3.3 t/h. The recovery rate of the concentrated water should be between 50~70%. Membrane concentration processes such as ED and DTRO can be used to further concentrate the salt to about 12~15%.
3.1.3. Thermal flue gas concentration + Spray drying evaporation. Applicable Scope:
Desulfurization wastewater per 100MW unit is > 3.3 t/h. The recovery rate of concentrated water should be above 70%. Thermal concentration and other processes should be selected to concentrate the salt content to 15-20%.

There are two kinds of low-temperature flue gas concentration processes: "in the flue" and "bypass tower". Compared with membrane method, MVR, MED and other concentration processes, the complex pretreatment system can be cancelled, with lower investment and operating cost.

3.2. Process comparison and cost accounting
Compared with evaporative crystallization technology, flue gas treatment of desulphurization wastewater has obvious advantages, and its investment cost and operation cost are obviously lower than the traditional evaporative crystallization method. As shown in table 1.

Table 1. Technical comparison and cost accounting of evaporative crystallization technology and flue gas evaporation technology.

| The serial number of power plant | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10   |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Technology Combination          | Self-crystallization flash process+flue gas waste heat utilization | Partial softening+NF+ED+RO+MVR | All softened+RO+NF+MVR | All softened+RO+FO+ash field spraying | All softened+RO+NF+RO+MVR | All softened+RO+flue gas evaporation | All softened+MED | All softened+FO+TVC | Low temperature gas concentration+high temperature gas drying |
| Treatment capacity (t/h)        | 30  | 20  | 20  | 25  | 20  | 36  | 20  | 20  | 22  | 10   |
| Concentrate quantity (t/h)      | 4   | 0.09| 0.1 | 4   | 0.1 | 8   |     |     |     |      |
| Disposal of concentrated solution | Dry in flue | Coal yard | Spray drying | The ash field | Coal yard and ash field | By-pass flue drying | Low temperature flue gas drying |
| Secondary products              | Mixed salt to ash | Calcium sulfate, sodium chloride | Sodium chloride | Spray to the ash field | Sodium chloride | Sodium chloride | Mixed salt to ash | Sodium chloride | Mixed salt to ash |
| Investment cost (ten thousand yuan/t) | 162 | 200 | 194 | 120 | 160 | 239 | 175 | 487 | 386 | 149   |
| Operating cost (yuan/t)         | 7.80 | 26.75 | 60.59 | 50.45 | 48.03 | 33.85 | 23.12 | 70  | 38.7 | 15    |
| Power consumption (yuan/t)      | 7.80 | 7.8 | 11.8 | 3.24 | 6.24 | 13.67 | 5.83 | 13  | 3.8  | 6.77   |
| Pharmaceutical cost (yuan/t)    | 0 | 18.95 | 43.41 | 42.21 | 38.8 | 19.62 | 10  | 23  | 12.9 | 0     |
| Steam consumption (yuan/t)      | 0 | 0 | 4.8 | 5 | 0 | 0.56 | 0 | 34  | 22  | 0     |
| Other consumption (yuan/t)      | 0 | 0 | 0.58 | 0 | 2.99 | 0 | 7.29 | 0.58 | 0 | 8.23 |

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At present, the new zero-discharge wastewater process includes a combination of treatment process sections with "pretreatment", "membrane system" concentration, RO filtration, and "vertical falling-film MVR evaporator" evaporation and crystallization as the core. This process can realize the waste water recycling, no liquid waste from the factory, but the investment cost of wastewater treatment for 2-3.5 million yuan/t of water, running cost 30-120 yuan/t of water. The high investment and operation cost of the above mentioned zero-discharge wastewater is difficult for small and medium-sized power plants to load, so a low-cost zero-discharge wastewater solution should be sought.

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