Experimental study on the treatment of desulfurization wastewater from coal-fired power plant by spray evaporation

Zongkang Sun

Guangdong Power Grid Corp Electric Power Research Institute

Ning Zhao

Guangdong Power Grid Corp

Yongxin Feng

Guangdong Power Grid Corp

Fengjun Liu

Southeast University

Chenjian Cai

Southeast University

Guangmin Che

Southeast University

Yaping Zhang

Southeast University

Hao Wu

Nanjing Normal University

Linjun Yang (✉ ylj@seu.edu.cn)

Southeast University

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Abstract

The desulfurization wastewater in coal-fired power plants is difficult to treat due to its high salt concentration and complex composition. In this study, a pilot-scale evaporation tower system was built to treat the desulfurization wastewater by spray evaporation. The distribution characteristics of Cl^- in wastewater evaporation process, the characteristics of solid evaporation products from desulfurization wastewater and the influence on the characteristics and removal effect of particulate matters in flue gas were investigated. The results show that the increase of salt content in desulfurization wastewater increased the mass concentrations of Cl^- in the gas phase, outlet solid phase and bottom solid phase, but the proportions of it in three phases remained almost unchanged. The increase of flue gas temperature can improve the content of Cl^- in the gas phase, while the increase of wastewater pH inhibited the formation of gaseous HCl . The solid evaporation products from desulfurization wastewater had prismatic crystal structure, which mainly included the sulfate and chloride salts, and the main elements in them were O, Na, Mg, S, Cl, K and Ca. Besides, the particle size of bottom solid phase was larger than that of outlet solid phase. For the particulate matters in flue gas, the spray evaporation of desulfurization wastewater can reduce the particle concentration, promote the particle agglomeration, reduce the number concentration of fine particles and improve the removal effect of PM_{10} .

1. Introduction

At present, the limestone–gypsum wet flue gas desulfurization (WFGD) technology has become the main method for flue gas desulfurization in coal-fired power plants. This technology has the advantages of high maturity, stable operation and good adaptability to different working conditions. Meanwhile, there are abundant desulfurizer resources, and the desulfurization product (CaSO_4) can be comprehensively utilized (Brogren and Karlsson 1997; Dong et al. 2017; Bogacki et al. 2018). However, in order to maintain the crystallization rate of CaSO_4 and the normal operation of desulfurization system, a certain amount of desulfurization wastewater needs to be discharged regularly to ensure the concentration of chloride ion (Cl^-) in the desulfurization slurry is lower than the limit value. Generally, the Cl^- concentration in desulfurization slurry should be maintained lower than 20000 ppm to prevent the equipment corrosion (EPA 2009). The desulfurization wastewater has high salt concentration, complex composition and great difficulty in treatment (Conidi et al. 2018; Huang et al. 2017). The current treatment methods for desulphurization wastewater mainly include the chemical precipitation (Fang et al. 2018; Chen et al. 2018; Jia and Wang 2018; Yan et al. 2019), membrane separation (Lee, Kim and Hong 2018), evaporative crystallization (Liang et al. 2018), electrodialysis (Tanaka 2006), biological treatment (Wei et al. 2017) and spray evaporation (Ma et al. 2016; Han et al. 2020). At present, the chemical precipitation is the most commonly used method for desulfurization wastewater treatment in coal-fired power plants, but it needs high investment and operation cost, and can't remove chloride ions effectively. Compared with that, the spray evaporation technology has prominent advantages in investment and operation cost, so it has attracted much attention in recent years.

The spray evaporation technology is to atomize the liquid into small droplets firstly, and then evaporate them using hot air. The atomization of liquid increases its surface area, thus improving the heat and mass transfer between liquid and hot air, which is conducive to its rapid evaporation. It is widely used in pharmaceutical, food, flavor and chemical industries (O'Sullivan et al. 2019; Sollohub et al. 2010; Anwar and Kunz 2011; Tsetsekou et al. 2001), but there are less practical applications in desulfurization wastewater treatment until now. For the spray evaporation of desulfurization wastewater, it is firstly atomized into droplets with small sizes, and then the hot flue gas from the end of the boiler is extracted to evaporate the wastewater droplets rapidly, so as to realize the zero liquid discharge (ZLD) of it. The spray evaporation of desulphurization wastewater includes two modes, one is the flue evaporation technology and the other is the evaporation tower technology. The flue evaporation technology is to spray atomized droplets into the main or bypass flue between air preheater and electrostatic precipitator (ESP), and make use of the hot flue gas to evaporate them (Fu et al. 2018; Feng et al. 2019; Ma et al. 2020). Due to the low temperature of flue gas between air preheater and ESP, when the boiler load changes, it is easy to cause incomplete evaporation of desulfurization wastewater and result in corrosion of flue and equipment. At the same time, the promotion of low-temperature economizer shortens the length of flue that can be used for evaporation, which also aggravates this risk (Li et al. 2019). The evaporation tower technology is to spray the atomized desulfurization wastewater into an evaporation tower, which is arranged in a bypass flue before air preheater. Part of the flue gas is extracted from the main flue before air preheater and enters into the tower to evaporate the wastewater droplets (Zhang et al. 2019; Zheng et al. 2019; Ma et al. 2019). The temperature of flue gas before air preheater is high, the volume of evaporation tower is large and the flue gas velocity in it is low, so the heat transfer between the droplets and flue gas is enhanced and the evaporation time is prolonged, which can ensure the complete evaporation of droplets before they flow out of the tower. Besides, the volume of hot flue gas extracted from the main flue can be easily adjusted during operation, so it has good adaptability to the change of boiler load and is more suitable for the desulfurization wastewater treatment. Zhang et al. (2019) analyzed the effects of four main factors on the evaporation efficiency of desulfurization wastewater, such as the initial diameter distribution, mass flow rate of flue gas, flow gas temperature and humidity in the evaporation tower. Zheng et al. (2019) used two typical types of industrial desulfurization wastewater to study the change rule of pH and total dissolved solids during wastewater concentration in a circulating evaporation tower. Ma et al. (2019) reported the evaporation performance of desulfurization wastewater and the characteristics of evaporation products based on the evaporation tower technology, and a comprehensive discussion of the impacts on the existing equipment was made.

The evaporation of desulfurization wastewater will produce gaseous and solid evaporation products. The volatile ions in desulphurization wastewater can partly volatilize into the flue gas, and the other ions crystallize and precipitate out as solid particles. Cl^- is the main volatile ion in desulfurization wastewater, and some of Cl^- volatilize into the flue gas in the form of hydrogen chloride (HCl), which may cause corrosion to downstream equipment with the decrease of flue gas temperature. Meanwhile, the precipitated solid particles also enter the flue gas and mix with the fly ash particles from coal combustion, which may affect the characteristics of particulate matters in flue gas. In order to ensure the

normal operation of the spray evaporation system, it is necessary to study the characteristics and influence of evaporation products from desulfurization wastewater. Ma et al. (2018) carried out the research on chloride ion gas–solid distribution in the process of desulfurization wastewater evaporation, and the factors analysis on the gas–solid phase distribution coefficient of chloride ion was detected. Liang et al. (2017) dealt with the thermodynamic and chemical studies of the evaporation and crystallization in the desulfurization wastewater droplets. Zheng et al. (2019) explored the chlorine migration of various chlorine salt solutions and typical desulfurization wastewater at high temperature during the evaporation process of concentrated wastewater by a laboratory-scale tube furnace and a pilot-scale system. However, few studies have been conducted on the characteristics of gaseous and solid evaporation products from actual desulfurization wastewater in the process of spray evaporation, as well as the influence on the characteristics and removal effect of particulate matters in original flue gas.

In this study, a pilot-scale evaporation tower system was built to treat the desulfurization wastewater from coal-fired power plant by spray evaporation. The distribution characteristics of Cl^- in wastewater evaporation process were investigated by experiments, including the effect of flue gas temperature and wastewater pH on its distribution. The morphology, elements, components and size distribution of solid evaporation products from desulfurization wastewater were investigated respectively. In addition, the influence of wastewater spray evaporation on the concentration, morphology and elements of particulate matters, as well as the size distribution and removal effect of PM_{10} (particles with aerodynamic diameter less than $10\text{ }\mu\text{m}$) in flue gas was also investigated. This work can provide a reference for the treatment of desulfurization wastewater in coal-fired power plants.

2. Experimental Section

2.1. Experimental set-up

The schematic of evaporation tower system for desulfurization wastewater treatment is shown in Figure 1. In this system, the air was heated by the gas heater, then entered the buffer vessel, evaporation tower and ESP in turn, and finally discharged by the induced draft fan. In the buffer vessel, the coal-fired fly ash was added by a solid aerosol generator to adjust the concentration of particulate matters in flue gas. In the evaporation tower, the desulfurization wastewater was firstly atomized by a rotary atomizer, which was arranged at the top of the tower and composed of a motor and an atomizing disc. The motor drove the atomizing disc to rotate at a high speed, and 12 orifice channels were evenly arranged along the circumference in it. Through the high-speed rotation of atomizing disc, the desulfurization wastewater was stretched into a thin liquid film at the edge of the disc and then was split into small droplets for evaporation. The desulfurization wastewater was stored in a wastewater tank and fed into the rotary atomizer by a metering pump. The evaporation tower was 1.6 m in diameter and 6.0 m in height, which was cylindrical in the middle and tapered at the bottom (Figure 2(a)). Besides, it also contained a gas distributor, shown in Figure 2(b). The gas distributor mainly consisted of the gas inlet, volute, inner flow

channel, outer flow channel and several deflectors, and the atomizing disc was located directly below the gas distributor. The flue gas firstly entered into the volute from the inlet and flowed spirally in it. Then the flue gas entered the inner and outer flow channels, and it spiraled downward into the tower under the action of deflectors. After contacting with the droplets from the atomizing disc, the flue gas carried them spiraling downward together, which prolonged the residence time of droplets in the tower and was conducive to their complete evaporation. After the evaporation, some large particles precipitated from desulfurization wastewater would deposit at the tower bottom under the centrifugal force and gravity, other small ones would flow out from the tower with flue gas and be removed by the ESP.

During the experiment, the flue gas temperature in front of the evaporating tower was controlled at 350°C, the flue gas volume was 600 Nm³/h, the wastewater flow rate was 50 L/h, and the atomizer rotating speed was 18000 r/min. The ESP was a barb-plate tube type and the working voltage was -40 kV. In addition, the aspirated isokinetic sampler (WJ-60B, Laoying Ltd., China) was applied to collect the solid evaporation products or ash samples from the flue gas, and the electrical low pressure impactor (ELPI+, Dekati Co. Ltd., Finland) was applied to measure the concentration and size distribution of PM₁₀ in flue gas, which can measure particles from 6 nm to 10 μm in real time. The concentration of gaseous HCl in flue gas was measured according to the standard of ASTM D7773-12, in which the solution absorption method was applied and the concentration of Cl⁻ in the solution was measured by an ion chromatograph (Dionex ICS-2100, Thermo Fisher Scientific, USA). The morphology of solid evaporation products and ash samples was observed by a field emission scanning electron microscopy (Ultra Plus, Zeiss Ltd., Germany), which also contains an energy dispersive spectrometer (EDS) and can measure the element composition of them. The components of solid evaporation products were detected by an X-ray diffractometer (XRD) (X'pert PRO, PANalytical B.V., Netherlands). The size distribution of solid evaporation products was measured by a laser particle size analyzer (BT-9300ST, Baite Ltd., China).

2.2. Characteristics of desulfurization wastewater

The desulfurization wastewater used in the experiment was taken from three different coal-fired power plants. According to the salt content in the wastewater, it was divided as low-salinity, medium-salinity and high-salinity wastewater. The compositions of desulfurization wastewater from three coal-fired power plants are shown in Table 1, and it can be seen that the three kinds of desulfurization wastewater were all weak acidic, in which the Cl⁻ and SO₄²⁻ were the main anions, Mg²⁺ and Ca²⁺ were the main cations. The atomization characteristics of three kinds of desulfurization wastewater by the rotary atomizer are shown in Figure 3, and the size distribution of atomized droplets was measured by a particle dynamic analyzer (PDA, Dantec Dynamics Co. Denmark). It shows that with the increase of salt content in wastewater, the average size of atomized droplets (D_{32}) gradually increased, but all droplet sizes were less than 50 μm, which indicated that the atomization effect was good, and the rotary atomizer had good adaptability to desulfurization wastewater with different salt contents.

Table 1
Compositions of desulfurization wastewater from three coal-fired power plants.

Wastewater	pH	TDS (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	K ⁺ (mg/L)	Na ⁺ (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)
Low-salinity	6.5	19790	3940	4897	1625	1210	3790	2503
Medium-salinity	6.4	67234	13489	18751	5524	3930	10790	7804
High-salinity	6.2	139020	24981	27627	9523	6137	34575	11301

3. Results And Discussion

3.1. Distribution characteristics of Cl⁻

3.1.1. Distribution of Cl⁻ in three kinds of desulfurization wastewater after evaporation

During the evaporation process, some chloride ions in desulfurization wastewater volatilize in the form of HCl to form gaseous evaporation products, and the others stay in the solid evaporation products to form chloride salts. In order to study the distribution characteristics of Cl⁻, the distribution of Cl⁻ in three kinds of desulfurization wastewater after evaporation was tested, and the results are shown in Figure 4. In the experiment, the solid aerosol generator was turned off and there was no fly ash in the flue gas. When the experimental conditions were stable, a certain volume of flue gas was extracted from the outlet of the evaporation tower by the aspirated isokinetic sampler. The solid evaporation products in it were filtered and the flue gas was absorbed by NaOH solution, then the concentration of Cl⁻ in the solution was measured to calculate the mass concentration of it in the gas phase, which is expressed as follows:

$$c_{gas} = \frac{c(Cl^-)_1 \times V(NaOH)}{V_s}$$

1

where c_{gas} is the mass concentration of Cl⁻ in the gas phase, $c(Cl^-)_1$ is the concentration of Cl⁻ in the NaOH solution, $V(NaOH)$ is the volume of NaOH solution, V_s is the volume of sampled flue gas.

Similarly, the filtered solid evaporation products were dissolved in deionized water, then the concentration of Cl⁻ in the solution was measured and the mass concentration of it in the outlet solid phase was obtained as follows:

$$c_{outlet} = \frac{c(Cl^-)_2 \times V_d}{V_s}$$

2

where c_{outlet} is the mass concentration of Cl^- in the outlet solid phase, $c(Cl^-)_2$ is the concentration of Cl^- in the deionized water solution, V_d is the volume of deionized water solution, V_s is the volume of sampled flue gas.

Besides, a part of evaporation products with large sizes fell to the tower bottom and didn't flow out from the outlet. Therefore, the mass concentration of Cl^- in the bottom solid phase was obtained by subtracting that in the gas phase and outlet solid phase from the total amount of Cl^- in the desulfurization wastewater, given by

$$c_{bottom} = \frac{c(Cl^-)_w \times V_w}{V_T} - c_{gas} - c_{outlet}$$

3

where c_{bottom} is the mass concentration of Cl^- in the bottom solid phase, $c(Cl^-)_w$ is the concentration of Cl^- in the wastewater, V_w is the wastewater flow rate (50 L/h), V_T is the flue gas volume (600 Nm³/h).

The results show that with the increase of salt content of desulfurization wastewater, the mass concentrations of Cl^- in the gas phase, outlet solid phase and bottom solid phase all increased. The volatilization mechanism of Cl^- into gas phase is as follows (Ma et al. 2019; Ma et al. 2018):

There are two sources of HCl in the gas phase, one is the combination of H^+ and Cl^- in the desulfurization wastewater (reaction (4)), and the other is the hydrolysis of chlorine salts precipitated from desulfurization wastewater at high temperature (reaction (5)-(7)). Reaction (4) is the main volatilization mechanism, and reaction (5)-(7) can only occur at high temperature with low reaction intensity. With the increase of salt content in the desulfurization wastewater, the content of Cl^- in it also increased, which was conducive to the reaction (4), thus increasing the mass concentration of HCl in the gas phase.

On the other hand, the precipitation mechanism of Cl^- is as follows:

With the gradual evaporation of water in the wastewater droplets, the Cl^- combines with the cations in the desulfurization wastewater to form chloride salts. It can be seen that the increase of Cl^- in desulfurization wastewater can also promote the formation of chloride salts in reaction (8), so the mass concentration of Cl^- in solid phase also increased.

However, although the increase of salt content in desulfurization wastewater increased the mass concentrations of Cl^- in gas and solid phase, the proportions of it in the gas phase, outlet solid phase and bottom solid phase remained almost unchanged. This is due to that the desulfurization wastewater evaporated in the form of atomized droplets when it was sprayed in the evaporation tower. For a single wastewater droplet, the evaporation process includes two stages. The first stage is similar to the evaporation of pure water droplet. Due to the high water content, the main reaction in this stage is the water evaporation, and the evaporation speed is very fast. The second stage is similar to the drying process of hydrous particulate matters. With the decrease of water content in the droplet, the desulfurization wastewater is concentrated, and the ion concentration increases, accompanied by the volatilization and precipitation of ions. For different desulfurization wastewater, the atomization droplets were all firstly concentrated to a high ion concentration in a short time, and then the volatilization and precipitation of Cl^- happened, so the volatilization and precipitation mechanism of Cl^- is the same. Therefore, the salt content in the desulfurization wastewater didn't affect the final distribution ratio of Cl^- in the gas phase, outlet solid phase and bottom solid phase.

3.1.2. Effect of flue gas temperature on the distribution of Cl^-

In the evaporation process of desulfurization wastewater droplets, the flue gas temperature is an important factor, and the effect of flue gas temperature on the distribution of Cl^- was investigated, illustrated in Figure 5. The medium-salinity wastewater was used in this experiment, and the flue gas temperature in front of the evaporating tower was adjusted to 280, 300, 320, 340 and 360°C by the gas heater. It can be seen from the results that with the increase of flue gas temperature, the content of Cl^- increased in the gas phase and bottom solid phase, while that in the outlet solid phase decreased significantly. Otakar (2000) studied the change of pure water pH with the temperature, and found that with the increase of temperature, the pH of water decreased, indicating that the rise of temperature made water acidified and it can ionize more H^+ . Therefore, with the increase of flue gas temperature, the content of H^+ in the wastewater droplets increased, which promoted the reaction (4) and increased the content of Cl^- in the gas phase. At the same time, the increase of temperature can promote the hydrolysis of chlorine salt (reaction (5)-(7)), thus also increasing the content of Cl^- in the gas phase. Correspondingly, the total content of Cl^- in the solid phase would decrease due to the mass conservation. However, the rise of flue

gas temperature can promote the rapid evaporation of droplets and lead to the accelerated precipitation of solid evaporation products, which would enlarge the sizes of them.³⁰ With the increase of their sizes, more solid evaporation products can deposit at the bottom under the centrifugal force and gravity, so that the content of Cl^- in the bottom solid phase increased slightly. On the other hand, the total content of Cl^- in the solid phase decreased and less solid evaporation products can flow out from the tower, so the content of Cl^- in the outlet solid phase decreased significantly.

3.1.3. Effect of wastewater pH on the distribution of Cl^-

The effect of wastewater pH on the distribution of Cl^- was also investigated, as shown in Figure 6. The medium-salinity wastewater was used in the experiment and the pH of it was adjusted to acidic (pH=3), neutral (pH=7) and weak alkaline (pH=10) with HNO_3 or $\text{Ca}(\text{OH})_2$, respectively. The results show that with the increase of wastewater pH, the content of Cl^- in gas phase decreased, while that in the outlet solid phase and bottom solid phase both increased, and it increased significantly in the outlet solid phase. It can be seen from the reaction (4) that the H^+ in desulfurization wastewater can promote the formation of gaseous HCl , but with the increase of wastewater pH, the content of H^+ decreased, which inhibited the formation of gaseous HCl and caused the decrease of Cl^- in gas phase. Correspondingly, the total content of Cl^- in the solid phase increased. In addition, after precipitated from desulfurization wastewater, the solid evaporation products with large sizes would settle to the tower bottom and remain in the flue gas with high temperature, while those with small sizes would flow out from the tower quickly with the flue gas. Therefore, the chloride salts in the bottom solid phase stayed for a long time in the high-temperature flue gas, which intensified the hydrolysis of them and made the content of Cl^- less than that in the outlet solid phase. Accordingly, the change of Cl^- content in the bottom solid phase with the wastewater pH was also not as obvious as that in the outlet solid phase. The HCl in the gas phase will cause corrosion in the flue and equipment when the flue gas temperature decreases, which is not conducive to the safe operation of the system. As a result, it can be considered to use alkaline substances (*e.g.*, $\text{Ca}(\text{OH})_2$) to adjust the pH of desulfurization wastewater before evaporation, so as to inhibit the formation of gaseous HCl and prevent the corrosion of flue and equipment.

3.2. Characteristics of solid evaporation products from desulfurization wastewater

3.2.1. SEM, EDS and XRD analysis of solid evaporation products

The evaporation of desulfurization wastewater can produce solid particles with different sizes, which are the salts formed by the precipitated ions. In the evaporation tower, a part of the solid evaporation products and fly ash particles with large sizes settled to the tower bottom, and the other part of them flowed out from the tower with flue gas and were captured by the ESP. That is, almost all the solid evaporation products will be mixed into the fly ash eventually, which may affect the resource utilization of

it. Therefore, the characteristics of solid evaporation products precipitated from desulfurization wastewater were investigated, and the SEM, EDS and XRD analysis of them were carried out to explore their morphology, elements and components, as shown in Figure 7. Besides, the relevant characteristics of coal-fired fly ash were also detected as comparison, which was taken from a coal-fired power plant. Figure 7(a) shows the morphology of coal-fired fly ash. It can be seen that a large number of spherical particles with different sizes existed in it, and there was no obvious connection between them. Figure 7(b) shows the morphology of solid evaporation products. In the experiment, the medium-salinity wastewater was used, the fly ash was not added in the flue gas and the solid evaporation products from wastewater were sampled from the tower bottom. It can be seen that the solid evaporation products of desulfurization wastewater had prismatic crystal structure, and the crystals connected with each other very tightly, which was completely different from that in fly ash. The elements of fly ash and solid evaporation products are illustrated in Figure 7(c). The results show that the main elements in fly ash were C, O, Al, Si, and the contents of other elements were very low. While, the main elements in solid evaporation products were O, Na, Mg, S, Cl, K and Ca, which was consistent with the compositions of desulfurization wastewater in Table 1. The components of fly ash and solid evaporation products are shown in Figure 7(d). It can be seen that the fly ash were mainly comprised of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, Al_2O_3 , SiO_2 , CaO and MgO. While, except for the $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and Al_2O_3 , the KCl, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, MgSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, CaSO_4 and NaCl were also detected in the solid evaporation products. Compared with the compositions of desulfurization wastewater in Table 1, it indicated that the anions and cations in the wastewater precipitated out to form solid evaporation products, which mainly included the sulfate and chloride salts.

3.2.2. Size distribution of solid evaporation products

The size distribution of solid evaporation products was also measured, which included that in the outlet and bottom solid phase, and the size distribution of fly ash was also measured for comparison, as shown in Figure 8. The size distributions of them were measured by a laser particle size analyzer, and the results were the volume distributions. It can be seen that the size distribution range of fly ash particles was wide, and all particle sizes were less than 200 μm . However, the size distributions of solid evaporation products were quite different from that of fly ash. For the outlet solid phase, the particle size distribution was unimodal, the peak value of it was at 0.32 μm and most of the precipitated particles were below 1.0 μm . For the bottom solid phase, the particle size distribution was also unimodal, but the peak value of it was at 7.67 μm and the particles distributed in the range of 5–200 μm , which indicated that the particle size of bottom solid phase was larger than that of outlet solid phase. The movement of particles in flue gas is mainly determined by their gravity and the drag force from flue gas (Spalding 1953). The mass of large particles in the solid evaporation products was large, so they were easy to deposit to the tower bottom under gravity. While, the particles with smaller sizes in the solid evaporation products had smaller mass and inertia, leading to better following performance to the flue gas, so they tended to flow out from the tower with flue gas. Therefore, the particle size of bottom solid phase was larger than that of outlet solid phase.

3.3. Influence on the particulate matters in flue gas

3.3.1. Concentration of particulate matters in flue gas

With the evaporation of desulfurization wastewater, some solid particles precipitated out from the droplets and mixed with the fly ash particles in flue gas, which may affect the characteristics of particulate matters in flue gas. Considering that, the concentration, morphology and elements of particulate matters in flue gas were investigated. The concentrations of particulate matters before and after the evaporation tower are shown in Figure 9. During the experiment, the coal-fired fly ash was added into the flue gas by the solid aerosol generator, and the particle concentrations at the tower inlet were adjusted to 7.62, 10.25 and 13.00 g/m³ (operating condition #1, #2 and #3), respectively. When the desulphurization wastewater was sprayed into the tower and evaporated stably, the particle concentration at the tower outlet was measured. The results show that with the increase of particle concentration at the tower inlet, it also increased at the tower outlet, but was less than that at the inlet. The particle concentrations at the tower outlet were 4.59, 5.41 and 6.32 g/m³ under operating condition #1, 2 and 3, respectively. After passing through the gas distributor, the flue gas rotated and flowed downward in the evaporation tower, making the fly ash particles and precipitated solid particles in flue gas also spiraled downward in it, which was similar to the cyclone separator. On one hand, the particles with larger sizes in flue gas settled to the tower bottom under gravity, and on the other hand, they did centrifugal movement in the horizontal direction under the drag force from flue gas, due to the large mass and inertia, they can easily be thrown to the tower wall under the centrifugal force and gradually settled to the tower bottom. Besides, some of the smaller particles in flue gas can collide with others to form large-size aggregates, thus also settling to the tower bottom. Therefore, the particle concentration in the flue gas at the tower outlet was lower than that at the tower inlet. Meanwhile, it can be seen that with the increase of particle concentration at the tower inlet, the particle concentration decrement was more obviously at the outlet. The separation efficiency was defined as the ratio of particle concentration decrement to the original particle concentration at the tower inlet, which were 39.76%, 47.22%, 51.38% under three operating conditions. It can be explained that with the increase of particle concentration in flue gas, the number of particles in unit volume increased, and the collision times between them also increased, which promoted the agglomeration effect of them. More particles in flue gas can agglomerate together and settle to the tower bottom under the gravity and centrifugal force, so as to separate from the flue gas and get a higher separation efficiency.

3.3.2. Morphology and elements of particulate matters in flue gas

The morphology and elements of particulate matters before and after the evaporation tower were illustrated in Figure 10. During the experiment, the particle concentration at the inlet of evaporation tower was 7.62 g/m³. Considering that the particulate matters in flue gas before the evaporation tower were fly ash particles, the morphology should be the same as that in Figure 7(a), so the detection was not

repeated here. Figure 10(a) shows the morphology of particulate matters after the evaporation tower. It can be seen that many spherical fly ash particles and prismatic crystals connected together to form large-size agglomerates, indicating that the fly ash particles in original flue gas collided and agglomerated with the solid evaporation products of desulfurization wastewater. The elements of particulate matters before and after the evaporation tower were illustrated in Figure 10(b). It can be seen that after the evaporation tower, the contents of Na, Mg, S, Cl, K and Ca in the particulate matters increased obviously, which were from the solid evaporation products of desulfurization wastewater. The results demonstrate that the spray evaporation of desulfurization wastewater in the evaporation tower can promote the agglomeration of particulate matters in flue gas and enlarge the sizes of them.

3.3.3. Size distribution of PM₁₀

A large number of particles with different sizes are produced in the coal combustion process, among which the particles with large sizes are easy to be removed by dust removal equipment. However, the removal efficiency of fine particles by existing dust removal equipment is relatively low due to their small sizes, making many of them escape into the atmosphere and cause serious environmental pollution. Consequently, the size distribution and removal effect of fine particles are very important for the pollutant control and environmental protection of coal-fired power plants. In order to further explore the influence of desulphurization wastewater spray evaporation on the particulate matters in flue gas, the size distributions and removal effect of PM₁₀ with and without the spray evaporation were investigated. During the experiment, the total particle concentration at the inlet of evaporation tower was maintained at 7.62 g/m³, and the size distributions of PM₁₀ were measured at the inlet and outlet of tower, as shown in Figure 11. The results show that it was a bimodal distribution of the PM₁₀ in original flue gas, and the particle peak diameters were 0.04 and 0.76 μm, where the particle number concentrations were $5.37 \cdot 10^6$ and $3.98 \cdot 10^6$ 1/cm³, respectively. After the spray evaporation of desulfurization wastewater, the PM₁₀ at the tower outlet was still bimodal, and the particle peak diameters remained the same. However, the particle number concentration decreased in each size range, and it decreased to $3.29 \cdot 10^6$ and $2.66 \cdot 10^6$ 1/cm³ at the particle peak diameters of 0.04 and 0.76 μm. It can be inferred that plenty of wastewater droplets were formed after the atomization, which would collide with the fly ash particles in the flue gas. Many fine particles adhered to the droplets and agglomerated together to form large aggregates, which can reduce the number of them. At the same time, the solid evaporation products just precipitated out from the wastewater droplets still contained a certain amount of moisture, the surfaces of which were wet and the fine particles were easy to adhere on them under the capillary force. With the continuous drying of solid evaporation products in the hot flue gas, many fine particles would connect with the prismatic crystals to form large aggregates, which can also reduce the number concentration of them.

3.3.4. Removal effect of PM₁₀ by ESP

The number and mass concentrations of PM₁₀ after ESP with and without the spray evaporation were also measured to investigate the influence on the removal effect of PM₁₀, illustrated in Figure 12. The

results show that the number and mass concentrations of PM_{10} after ESP were $1.87 \cdot 10^6$ $1/cm^3$ and 11.59 mg/m^3 without the spray evaporation of desulphurization wastewater. While, when the desulfurization wastewater was normally atomized and evaporated in the evaporation tower, the number and mass concentrations of PM_{10} after ESP decreased to $1.05 \cdot 10^6$ $1/cm^3$ and 7.33 mg/m^3 , which were reduced by about 43.8% and 36.8%, respectively. It indicated that the spray evaporation of desulphurization wastewater can improve the removal effect of fine particles in flue gas, thus reducing the concentration of PM_{10} after ESP. Many factors may affect the performance of ESP for fine particles, such as the particle characteristics, flue gas properties, equipment structures, operating conditions and electrical control peculiarities (White 1951). The spray evaporation of desulfurization wastewater mainly affected the particle characteristics in flue gas, including the particle size distribution and specific resistance. The spray evaporation of desulfurization wastewater can make the fine particles agglomerate and increase their sizes, so as to improve their charging performance in the electric field of ESP and promote their removal effect. On the other hand, the evaporation of desulfurization wastewater increased the flue gas humidity and reduced the temperature, thus reducing the specific resistance of fine particles, which was also conducive to the charging and removal of them.

4. Conclusions

In this work, a pilot-scale evaporation tower system was built to treat the desulfurization wastewater by spray evaporation. The distribution characteristics of Cl^- in wastewater evaporation process, the characteristics of solid evaporation products from desulfurization wastewater and the influence on the characteristics and removal effect of particulate matters in flue gas were investigated. The conclusions could be summarized as following:

- (1) The increase of salt content in desulfurization wastewater increased the mass concentrations of Cl^- in the gas phase, outlet solid phase and bottom solid phase, but the proportions of it in three phases remained almost unchanged. The increase of flue gas temperature can improve the content of Cl^- in the gas phase, while the increase of wastewater pH inhibited the formation of gaseous HCl.
- (2) The solid evaporation products from desulfurization wastewater had prismatic crystal structure, which mainly included the sulfate and chloride salts, and the main elements in them were O, Na, Mg, S, Cl, K and Ca. Besides, the size distributions of solid evaporation products in the outlet and bottom phases were both unimodal, and the particle size of bottom solid phase was larger than that of outlet solid phase.
- (3) The spray evaporation of desulfurization wastewater can reduce the particle concentration, promote the particle agglomeration, reduce the number concentration of fine particles and improve the removal effect of PM_{10} in flue gas.

Declarations

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Authors Contributions

Zongkang Sun: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing Original Draft.

Ning Zhao: Investigation, Review & Editing.

Yongxin Feng: Methodology, Resources.

Fengjun Liu: Conceptualization.

Chenjian Cai: Conceptualization.

Guangmin Che: Methodology.

Yaping Zhang: Review & Editing.

Hao Wu: Review & Editing, Supervision.

Linjun Yang: Review & Editing, Supervision.

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Competing Interests

The authors declare that they have no competing interests.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

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Figures

Figure 1

Schematic diagram of experimental set-up.

Figure 2

Structures of (a) the evaporation tower and (b) the gas distributor.

Figure 3

Size distribution of desulfurization wastewater droplets.

Figure 4

Distribution of Cl⁻ in three kinds of desulfurization wastewater after evaporation.

Figure 5

Effect of flue gas temperature on the distribution of Cl⁻.

Figure 6

Effect of wastewater pH on the distribution of Cl^- .

Figure 7

SEM, EDS and XRD analysis of solid evaporation products. (a) Morphology of ash; (b) morphology of solid evaporation products; (c) elements; (b) components.

Figure 8

Size distributions of solid evaporation products. (a) Differential distribution; (b) cumulative distribution.

Figure 9

Concentrations of particulate matters before and after the evaporation tower.

Figure 10

(a) Morphology and (b) elements of particulate matters before and after the evaporation tower.

Figure 11

Size distributions of PM₁₀ before and after the evaporation tower.

Figure 12

Number and mass concentrations of PM₁₀ after ESP with and without the spray evaporation.