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Experimental study on chlorine Migration of Desulfurization Wastewater in Hot Flue Gas Environment

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ABSTRACT

To study the migration law of chlorine in the hot flue gas environment of desulfurization wastewater. Based on the simulated experimental system of desulfurization wastewater evaporation, the composition and micro-morphology of gas-solid phase products during the evaporation of desulfurization wastewater are studied with the help of relevant analysis and testing instruments. The effects of different evaporation temperatures and pH values of desulfurization wastewater on the migration and transformation of chlorine in the process of desulfurization wastewater evaporation are also studied. The results show that gas-solid phase products are produced during the evaporation process of desulfurization wastewater, and the volatilization of chlorine increases with the increase of evaporation temperature, while the precipitation of chlorine decreases with the increase of pH value.

Keywords: Desulphurization wastewater, chlorine, migration and transformation

1. INTRODUCTION

The characteristics of energy reserves in China have been dominated by coal in the production and consumption of primary energy for a long time. In 2020, China's total energy consumption was 4.96 billion tons of standard coal, of which coal consumption accounted for 56.9% of primary energy, much higher than the global 27.2%[1]. Coal and other fossil fuels will release a large number of pollutants in the process of combustion, which will cause a variety of environmental problems. Therefore, in order to meet the requirements of environmental protection departments for flue gas emission from thermal power plants, limestone-gypsum desulfurization process has become the standard configuration of coal-fired power plants. However, in this process, Cl elements will be continuously enriched in the desulfurization slurry, resulting in the concentration of Cl^- in the desulfurization slurry will exceed the specified value. In order to reduce the concentration of Cl^- in the desulfurization slurry, it is necessary to discharge a part of the slurry regularly, which is the origin of desulfurization wastewater[2-5]. Part of HCl will be released in the process of desulfurization wastewater evaporation, and the removal efficiency of gaseous substances by dust collector is very low[6]. When chlorine volatilization is too large, it will increase the discharge of desulfurization wastewater; in addition, too high concentration of Cl^- in slurry will also have adverse effects on gypsum quality, desulfurization system corrosion and desulfurization efficiency[7].

Yu et al [8] conducted an evaporation experiment on wastewater from a power plant and found that the gaseous products evaporated in the flue of desulfurization wastewater mainly include: HCl, HF, HBr, HNO_2 and HNO_3, of which the volatile content of HCl is much higher than other components. Cui et al [9] studied the evaporation of desulfurization wastewater at medium temperature (250 °C-350 °C), and found that the medium temperature environment was more conducive to the evaporation of desulfurization wastewater, and the surface of the product was rough and porous, and the main products were NaCl, $CaSO_4 \cdot 0.5H_2O$ and $MgSO_4 \cdot H_2O$. Li et al [10] studied the migration of crystallized salt and chlorine in the process of evaporation of desulfurization wastewater at different temperatures, and found that flue gas temperature

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promoted the volatilization of HCl. Cui et al [11] simulated desulfurization wastewater prepared by $CaCl_2$ solution found that higher pH value was beneficial to reduce the emission of HCl.

In summary, the existing studies mainly focus on the evaporation characteristics, technical feasibility, flue evaporation process and evaporation products of desulfurization wastewater under different physical properties and operating conditions. However, there are few studies on the quality change of evaporation products and the law of chlorine transfer in the drying process of desulfurization wastewater. Reducing the volatilization ratio of chlorine plays an important role in reducing equipment corrosion and reducing the output of desulfurization wastewater. Therefore, it is of great practical significance to study the migration and transformation of chlorine in desulfurization wastewater in hot flue gas environment.

2. *MATERIAL AND METHODS*

2.1 Raw material

The composition analysis of the desulfurization wastewater is shown in Table 1: As shown in Table 1, the concentration of chloride ions and sulfate ions in the desulfurization wastewater is relatively high, and the desulfurization wastewater is weakly alkaline.

Table 1 Desulphurization wastewater composition

Index	Na^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	NO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	pH
Value	921	1847	704	383	4953	5596	7.37

2.2 Experimental system

Based on the desulfurization wastewater flue gas evaporation process, a simulation experiment system for desulfurization wastewater evaporation was designed and built, as shown in Figure 1. The system is mainly composed of an oil bath pan, a round bottom flask, a thermometer, a condenser, a collection bottle and an air pump. After the desulfurization wastewater is heated and evaporated in an oil bath at a constant temperature, the remaining solids remain at the bottom of the round-bottomed flask. The gaseous products such as HCl and water vapor enter the condenser with the airflow to condense and enter the collection bottle. The temperature of the oil bath can be adjusted to 300 °C, and the air volume flow of the air pump is set to 0.12 m^3/h.

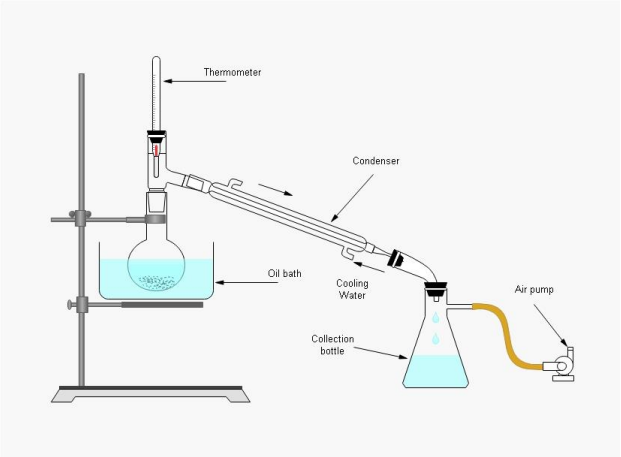

Fig 1 Schematic diagram of simulated experimental system for desulfurization wastewater evaporation

3. RESULTS AND DISCUSSION.

The composition of gas-solid phase products and the characteristics of solid phase micro-morphology in the process of desulfurization wastewater evaporation are analyzed, and the effects of evaporation temperatures and pH values on the migration and transformation of chlorine in the process of desulfurization wastewater evaporation are discussed. the research results have a certain guiding significance for the engineering application of wastewater spray drying technology.

3.1 Characteristics of evaporation products of Desulfurization Wastewater

In order to study the characteristics of evaporation products of desulfurization wastewater, the residual solid products at the bottom of round bottom flask were taken out after evaporation, and the elemental composition and morphology of the products were analyzed by SEM and EDS, as shown in the following figure 2 and 3.

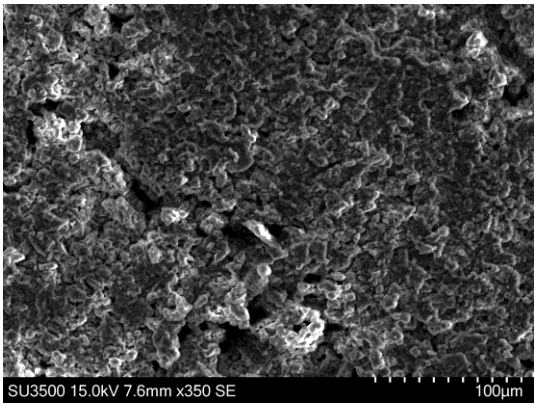

Fig 2 Micro-morphology of solid products from desulfurization wastewater evaporation

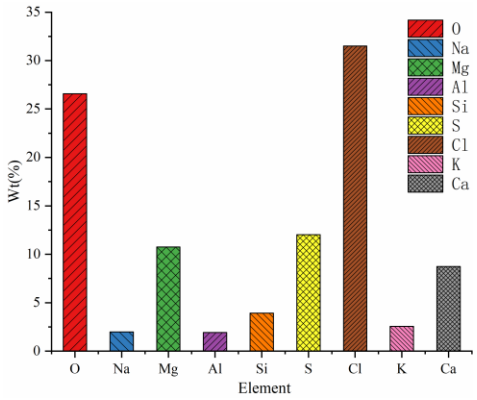

Fig 3 Element content of solid phase products from desulfurization wastewater evaporation

As shown in figure 2, it can be seen that the evaporation products of desulfurization wastewater mainly show long strips or columns of different sizes; from figure 3, it can be seen that the solid phase products of desulfurization wastewater after evaporation mainly contain O, Na, Mg, Al, Si, S, Cl, K and Ca elements.

3.2 Effect of evaporation temperature

The effect of different evaporation temperature on the precipitation amount and precipitation ratio of chlorine in gas-solid two-phase during the evaporation process of desulfurization wastewater, as shown in figures 4 and 5. When the evaporation temperature increases from 150 °C to 250 °C, the amount of HCl precipitation in the process of desulfurization wastewater evaporation increases from 12.5 mg/L to 300 mg/L, and the proportion increases from 0.25% to 6.06%, while the amount of solid chloride precipitation decreases from 4898 mg/L to 4319 mg/L. (The proportion of HCl precipitation refers to the ratio of the amount of HCl precipitated from evaporated 100 ml desulfurization wastewater to the amount of Cl^- in 100 ml desulfurization wastewater).

As can be seen from the above figure, the evaporation temperature has a greater impact on the migration characteristics of chlorine in the evaporation process of desulfurization wastewater.

$$H_2O \rightleftharpoons H^+ + OH^- \quad (1)$$

$$H^+ + Cl^- = HCl \quad (2)$$

Formula (1) and (2) are the volatilization mechanism of HCl in desulfurization wastewater. In the process of desulfurization wastewater evaporation, chloride ion usually exists in the form of HCl in the gas phase. with the increase of temperature, the chemical equilibrium shifts to the endothermic reaction, and the process of water separation is an endothermic process, so when the temperature increases, the equilibrium of formula (1) shifts to the right, so that the H^+ concentration in the solution increases, and the increase of H^+ concentration will promote the occurrence of the reaction. Therefore, the precipitation amount of HCl in desulfurization wastewater increases, and the proportion also increases.

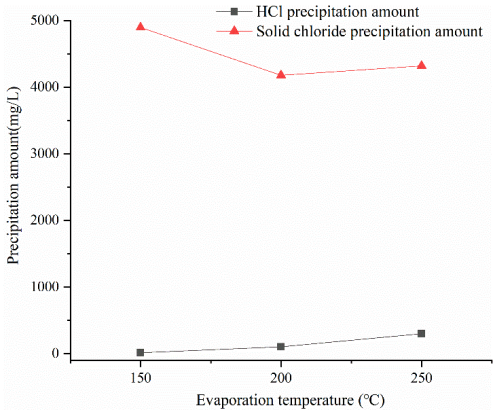

Fig 4 Effect of evaporation temperature on chloride precipitation in desulfurization wastewater

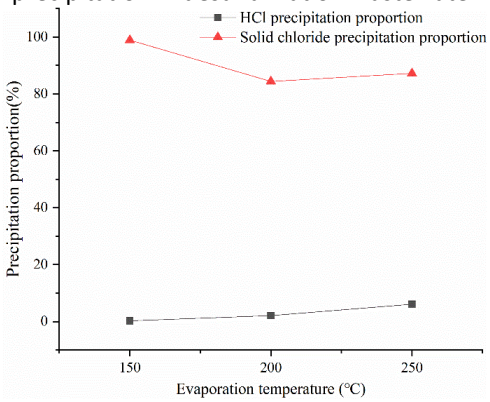

Fig 5 Effect of evaporation temperature on the proportion of chloride precipitation in desulfurization wastewater

3.3 Effect of pH value of Desulfurization Wastewater

The effect of different pH values on the precipitation amount and precipitation ratio of chlorine in gas-solid two-phase during the evaporation of desulfurization wastewater is shown in figures 6 and 7. When the evaporation temperature is controlled at 200 °C, when the pH value of desulfurization wastewater is changed from 4.01 to 10.06, the precipitation amount and proportion of HCl decrease obviously, while the precipitation amount and proportion of solid chloride increase.

It can be seen from the figure that at the same temperature, the amount of HCl released from desulfurization wastewater during evaporation decreases with the increase of pH value. This is because the precipitation of HCl is mainly affected by the concentration of H^+ and Cl^-. When the concentration of

Cl^- in the desulfurization wastewater is constant, the precipitation is mainly affected by the concentration of H^+. The lower the pH value of desulfurization wastewater is, the higher the H^+ concentration is, there is enough H^+ and Cl^- to combine to form HCl, and the acidic environment provides conditions for the existence of HCl; when the pH value of desulfurization wastewater is higher, the OH^- concentration is higher, the H^+ in the solution is less and Cl^- is relatively more, the formation of HCl decreases, and the alkaline environment also inhibits the existence of HCl. Therefore, the pH of desulfurization wastewater will affect the proportion of chlorine in gas-solid two-phase precipitation to a great extent.

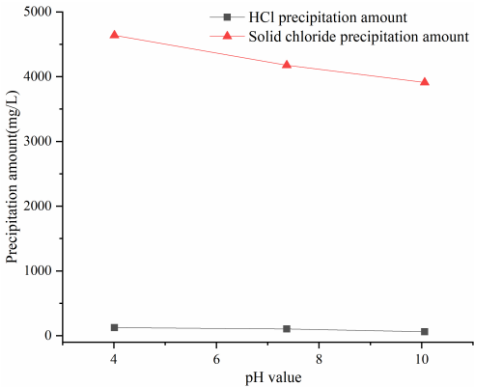

Fig 6 Effect of pH value on chlorine precipitation in desulfurization wastewater

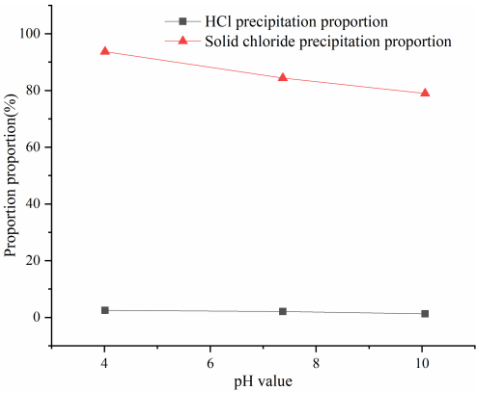

Fig 7 Effect of pH value on the proportion of chlorine precipitation in desulfurization wastewater

4. CONCLUSION

1. The micro-morphology of solid products from desulfurization wastewater evaporation is mostly long strip or column of different sizes, which mainly contains O, Na, Mg, Al, Si, S, Cl, K and Ca elements.

2. When the evaporation temperature increases from 150 °C to 250 °C, the amount of HCl precipitated from desulfurization wastewater increases from 12.5 mg/L to 300 mg/L, and the proportion increases from 0.25% to 6.06%, while the precipitation of solid chloride decreases from 4898 mg/L to 4319 mg/L. When the evaporation temperature is controlled at 200 °C, when the pH value is adjusted from 4.01 to 10.06, the amount of HCl precipitation and its proportion are significantly reduced, while the precipitation amount and proportion of solid chloride increase.

3. In practical engineering application, the evaporation temperature and pH value of desulfurization wastewater should be controlled to restrain the volatilization of HCl, so as not to affect the normal operation of the system.

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