Removal of elemental mercury and divalent mercury with ammonium sulfide in smelting gas containing SO_2

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Abstract. A set of simulation equipment is set up after the conditions of removing SO_2 and heavy metal Hg (Hg^0 and Hg^{2+}) has been investigated, the results of the removal technology method of absorption Hg^0, Hg^{2+} in smelting gases containing SO_2 with $(NH_4)_2S$ is tested, and their composition of reaction products and sediment are analyzed with XRD and XPS. Obtained that: when absorption concentration of $(NH_4)_2S$ are 0.8 mol/L, in pH 7.0-3.0 removal efficiency of Hg^0 and SO_2 is higher, temperature will affect the absorption of Hg^0, when reaction temperature is 30˚C the absorption of Hg^0 can be achieved the best. Under these optimum conditions, the removal efficiency of $Hg^{0,}$ Hg^{2+} and SO_2 could reach 89.45%, 99.42% and over 99.99%, the participation of SO_2 has a promote consequence on removal of Hg^0. The main reaction product is HgS, $HgSO_4$, $(NH_4)_2S_2O_3$.

Introduction

Non-ferrous smelting process would produce a large amount of flue gas, which main composition of smelting fumes are SO_2, SO_3, H_2O and heavy metals. Among them, Mercury is one of the most toxic heavy metals. In China, zinc smelting atmospheric mercury emissions reach to 49.1t, mercury emissions of Hg^0, Hg^{2+} and Hg^p is 78%, 17% and 5% of total mercury emissions respectively recent years. Hg^0 has gradually become a leading concern due to its high toxicity, it possesses high volatility and low solubility in water, and it is easily spread for a long time and long distances in the atmosphere. [1] The concentration of SO_2 is about 0.05% to 25% and SO_2 emissions constitute more than 8 percent of China's total SO_2 emissions [2].

For processing heavy metals from the flue gases, most research in internal and abroad, mainly by adsorption [3,4,5,6] and catalytic oxidation method [7,8,9]. But most of them either have a high economical cost or some of them have the problem of secondary pollution. Thus the developing of low costs and low pollution technology for mercury removal is still necessary. For the treatment of SO_2 smelting gas, there are related research in internal and abroad. This experiment chooses $(NH_4)_2S$ as absorbing liquid for the removal of SO_2, and it also has a relatively high absorption rate for Hg^{2+} and Hg^0. This paper focuses on the study of removal of bivalent mercury (Hg^{2+}), elemental mercury (Hg^0) and in simulated flue gas containing SO_2 by $(NH_4)_2S$ solution.

Experimental

Materials and methods

The experimental device for using ammonium sulfide to remove Hg^0, Hg^{2+} and SO_2 in simulated flue gas is shown in Fig.1. In this experimental, Hg^0, Hg^{2+} simulated flue gas was the mixed with SO_2 of single Hg^0 and Hg^{2+}. The corresponding tail gas absorption solution of Hg was acidic solution of $KMnO_4$, and the corresponding tail gas absorption solution of SO_2 was 5% NaOH. Because Hg^0 is easy to volatilize, u-shaped tube is used for generation of Hg^0. Dried compressed air is used to access into mercury vapor tube (Accounting for the total amount of oxygen is about 21%), flow rate is 10~20mL/min, inlet the mix bottle to mixed with SO_2. And for Hg^{2+}, put the soiled-state mercuric chloride ($HgCl_2$) into a tubular resistance furnace **(**SLG1200-60, 220V, 4000W**)**, then heated tubular resistance furnace to 400℃, then carrier gases were the mixture of nitrogen and sulfur dioxide with a constant flow rate of 200 mL/min. inlet concentration of Hg^0 is maintained at 20~40mg/m^3, inlet concentration of Hg^{2+} is 10~30 mg/m^3, which is correspond concentration of Hg^0 in smelting gases.

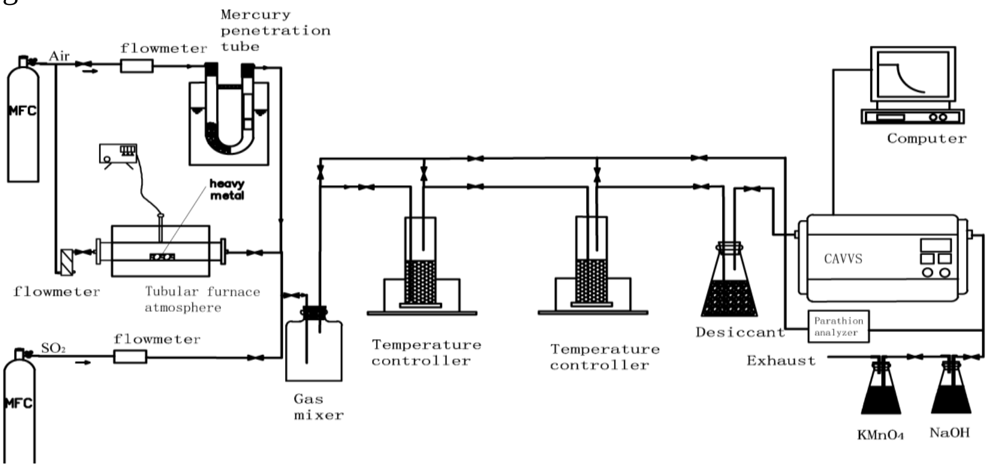

Fig.1 Simultaneously removal experimental device of absorbing smelting gas Hg^0, Hg^{2+} and SO_2 with $(NH_4)_2S$.

The experimental principle

The principle of Hg^{2+} removal can be fully explained by the equation ((Eq.1), Mercury ions (Hg^{2+}) reacted with sulfide ions (S^{2-}) to generate stable mercuric sulfide precipitate under the condition of weak alkaline, [10]. And as shown in (Eq.2-3), because of the existence of SO_2 in simulated flue gas react with the solution, and the reaction product between sulfur dioxide and ammonium sulfide, hydrogen sulfide (H_2S) and sulfur (S), can react with mercury (Hg^0), the principle of Hg^0 removal was shown in ((Eq.4-5).

Principle of $(NH_4)_2S$ absorb SO_2: According produces H_2S and no H_2S, the absorption process into pH> 7 stages and pH <Stage 7. And the overall reaction chemical equation is shown in Eq.2-3.

$$Hg^{2+} + S^{2-} \rightarrow HgS \downarrow \qquad (1)$$

$$6SO_2 + 4(NH_4)_2S + 4H_2O + O_2 \rightarrow 2(NH_4)_2S_2O_3 + 4NH_4HSO_4 + 2H_2S \qquad (2)$$

$$(NH_4)_2S_2O_3 + 2(NH_4)HSO_3 \rightarrow 2S + 2(NH_4)SO_4 + 2H_2O \qquad (3)$$

$$Hg^0 + S \rightarrow HgS \downarrow \qquad (4)$$

$$Hg^0 + H_2S \rightarrow HgS \downarrow + H_2 \qquad (5)$$

Results and discussion

Effect of $(NH_4)_2S$ absorption concentration on removal efficiency

Adding $(NH_4)_2S$ 100mL which concentration is 0, 0.2, 0.4, 0.8 and 1.0 mol/L respectively in absorption bottles, removal efficiency of Hg^0, Hg^{2+} and SO_2 are affected with concentration of $(NH_4)_2S$, the test results are shown in Fig.2. As can be seen from the Fig.2, when the concentration of $(NH_4)_2S$ solution was increased from 0 to 0.2 mol /L, the removal efficiency of Hg^0 also increased from 50.89% to 67.40%, removal efficiency of Hg^{2+} increased from 82.64% to 95.06% respectively, and the removal efficiency of SO_2 also increased from 88.7% to 98.8%. When the concentration of $(NH_4)_2S$ solution increased from 0.2 to 1.0mol, the removal efficiencies of Hg^0, Hg^{2+} and SO_2 could reach 87.71%, 99.96% and 99.92% respectively. As can be seen from equations (1-5), when the concentration of $(NH_4)_2S$ solution increased the concentration of S^{2-}, S and H_2S increased too.

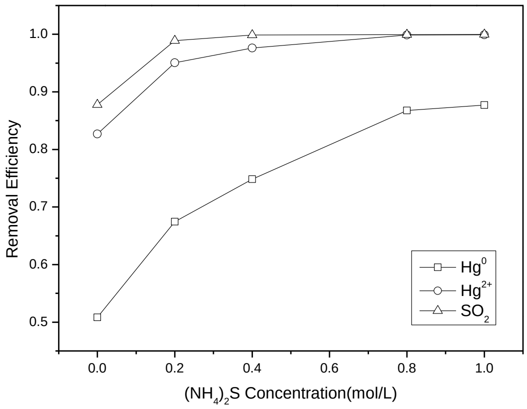

Fig.2 The influence of concentration on removal of mercury and SO_2 from simulated flue gas. (Concentration of SO_2 was 6%)

Effect of SO_2 absorption concentration on removal efficiency

Adjusting concentration of SO_2 gas to 0%, 2%, 4%, 6%, 10% respectively, removal efficiency of Hg^0, Hg^{2+} and SO_2 are affected with concentration of $(NH_4)_2S$, the test results are shown in Fig.3. As the concentration of SO_2 from simulated flue gas was increased from 0% to 2%, the removal efficiencies of Hg^{2+}, SO_2, decreased from 99.64%, 100%, to 99.05%, 99.99%, but the removal efficiencies of Hg^0 increased from 76.46% to 80.61% (Fig.3). When the concentrations of SO_2 from 2% to 10%, the removal efficiencies of Hg^0, Hg^{2+}, SO_2, decreased from 80.61%, 99.05% and 99.99% to 71.08%, 98.44% and 99.57%.The participation of SO_2 leads to pH of the solution is reduced, an acidic conditions more conducive to the absorption of Hg^0, and SO_2 react with $(NH_4)_2S$ solution produces S and H_2S can react with Hg^0. But as the reaction between SO_2 and $(NH_4)_2S$ proceeds are consuming solute, which makes removal efficiency of Hg^0, Hg^{2+} decline.

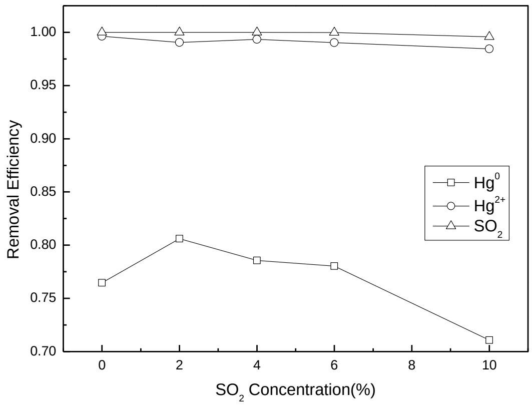

Fig.3 The influence of SO_2 on removal of mercury and SO_2 from simulated flue gas.

(concentration of $(NH_4)_2S$ was 0.8mol/L, temperature of $(NH_4)_2S$ was 20˚C)

The influence of pH value on removal efficiency

Continue experiment to be done in different pH, and averaging pH is used to observe the changes of pH value in absorption process, results are shown in Fig.4. As can be seen from Fig.4, when pH is from 12 to 7, absorption rate of Hg^0 increases from 48.89% to 74.67% with pH decrease. Acidic base of pH <7.0 is more beneficial to Hg^0's absorption, but the range of removal efficiencies for Hg^{2+} decrease, were 99.16%-97.14%, when the pH value was nearby 7, the removal efficiencies reduced to a minimum level. When pH is higher than 4.0 removal efficiency of SO_2 remains over 99.9%, pH has little effect on the absorption of SO_2. Gaseous Hg^0 can be dissolved into ions easier when the solution was acidic base, but when pH is reduced to below 3.0, absorption rate is low to 54.95% because of the $(NH_4)_2S$ solute consumption. But no matter under acidic or alkaline base, ions state of mercury (Hg^{2+}) can easily reacted with sulfur ions.

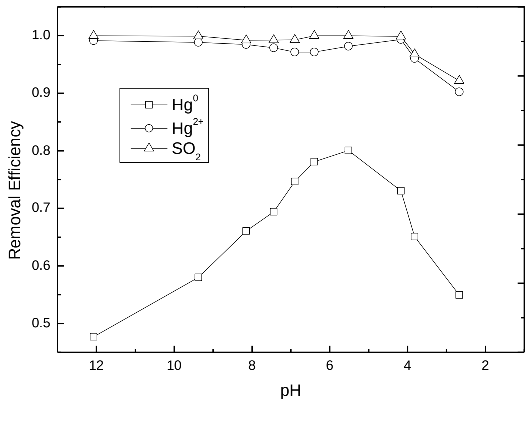

Fig.4 The influence of pH value on removal of mercury and SO_2 from simulated flue gas.

(Concentration of $(NH_4)_2S$ was 0.8mol/L, concentration of S O_2 was 6%, temperature of $(NH_4)_2S$ was 20˚C)

The influence of temperature on removal efficiency

Place $(NH_4)_2S$ 100mL which concentration is 0.8mol/L in absorption bottles of series two stage absorption, continue experiment in different reaction temperature (20˚C,30˚C, 40˚C, 50˚C, 70˚C) respectively, results are shown in Fig.5. As can be seen from Fig.5, when the temperature increased from 20˚C to 30˚C, removal efficiencies of Hg^0 and Hg^{2+} both increased, reach to 89.45% and 99.42% when the temperature was increased from 30˚C to 70˚C, the removal efficiencies of Hg^{2+} were not significantly increased, and the removal efficiencies of Hg^0 turn to decreased to 71.43%, the removal efficiencies of Hg^{2+}, SO2 were not significantly increased. Due to a range of rise temperature due to the accelerated the molecular motion to some extent, but the removal efficiency of ascension, but for Hg^0, the rise of reaction temperature will promote its volatile, leading to removal efficiency decreased.

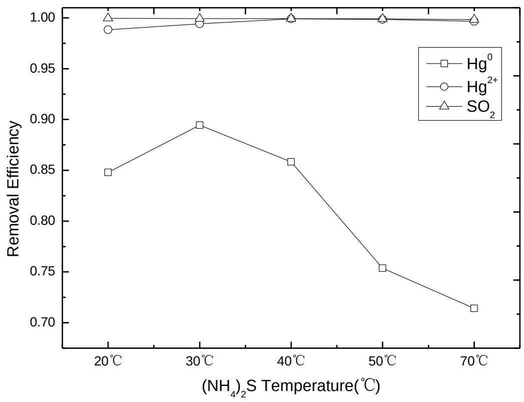

Fig.5 The influence of temperature on removal of mercury and SO_2 from simulated flue gas.

(Concentration of $(NH_4)_2S$ was 0.8mol/L, concentration of SO_2 was 6%, initial pH value of $(NH_4)_2S$ was 8)

Characterization of materials

XRD analysis

As shown in Fig.6 HgS characteristic peak is obvious that the reaction substance is the mercuric sulfide and have complete crystal shape, which proved that when solution absorb Hg^0 in the presence of SO_2 a small amount of black precipitates appears, and its composition is mainly HgS, it is same as Hg^{2+}.

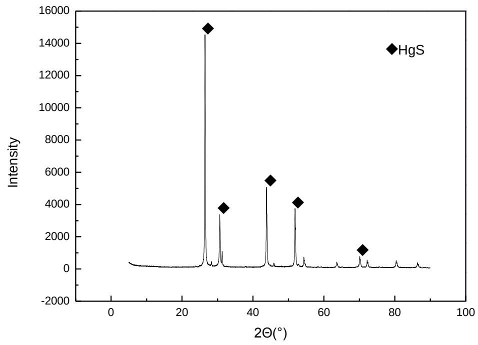

Fig.6 XRD patterns of $(NH_4)_2S$ removal Hg^0 generated precipitation.

XPS analysis

In order to further determine the products of reaction，XPS analysis was used to measure the kind and composition of the absorption liquid crystal, Analysis results show that in Fig.7. major S2p peaks centers at 168.78eV and 168.42eV, verify that the main form of products in solution is SO_4^{2-} and $S_2O_3^{2-}$.And the S2p 3/2 peak center 170.45 indicate the presence of H_2S. [11]

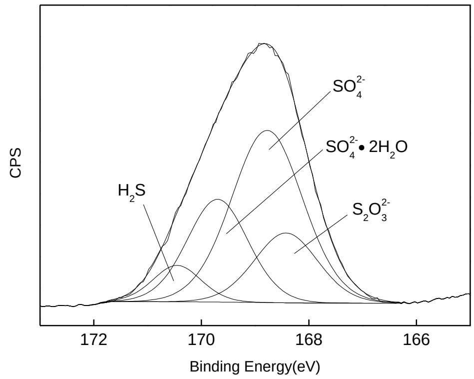

Fig.7 XPS patterns of absorbing liquid crystalline of $(NH_4)_2S$ removal of SO_2.

Conclusion

Considering removal efficiency and economic costs, to removal of Hg^0 and Hg^{2+} from metallurgical off-gas contains the SO_2 with $(NH_4)_2S$ as the absorption liquid, the optimal concentration, pH value and temperature of $(NH_4)_2S$ solution were 0.8 mol/L, 6 and 30℃ respectively. Under these conditions, the removal efficiencies of $Hg^{0,}$ Hg^{2+} and SO_2 from simulated flue gas could reach 89.45%, 99.42%, 99.99%, respectively. The results of XRD and XPS shows that the mechanism of Hg's removal was mainly chemical deposition, and the participation of SO_2 has a promote consequence on removal of Hg^0. The main products is likely to be HgS, $(NH_4)_2S_2O_3$, $(NH_4)_2SO_4$, and so on, it's ease of secondary use.

Acknowledgments

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