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Investigations on removal of SO_2 from flue gas by aerosol formation in pulsed corona discharge process*

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Abstract—The removal of SO_2 from flue gas by pulsed corona discharge in presence of ammonia was experimentally investigated. The results showed that the SO_2 removal mainly depends on thermal reaction of SO_2 with NH_3 and enhancements of 0%—25% by pulsed corona discharge in the range of the specific energy 0—5 Wh/Nm^3. The aerosol mass concentration, mainly composed of ammonium sulfate, increased with specific energy dissipated into the reactor. With an initial concentration of 2000—2100 ppmv SO_2 and energy consumption of 3 Wh/Nm^3, when a stoichiometric amount of ammonia is injected, the removal efficiency of SO_2 and percentage of ammonium sulfates in reaction products are all ≥80%. The collection efficiency of the reactor for aerosol is about 74% at a flue gas temperature of 60 to 65℃ and a water vapor content of 9% to 11% volume.

Keywords: pulse corona discharge; desulphurization of flue gas; collection of reaction products.

1 Introduction

Recent legislative efforts in China to reduce SO_2 emissions are mainly aimed at coal burned power plants. Although conventional scrubbing processes such as SO_2 neutralization by limestone seem to work adequately in facilities, these processes have various technical and economical disadvantages, especially for the solid waste emissions. Therefore, the development of low cost, flexible scrubbing procedures for SO_2 with no second solid waste emissions is an urgent task.

Removal of SO_2 from the flue gas by pulsed corona discharge in the presence of ammonia has been investigated by Masuda *et al*. (Masuda, 1987) and G. Dinell *et al*. (Dinell, 1990) as novel dry scrubbing process. This method basically uses high energetic electrons (5 to 20 eV) to generate OH, O_2H and O radicals in flue gas, then to oxidize SO_2, yielding the corresponding acid H_2SO_4. The reaction proceeds by a similar mechanism as that in smoggy atmospheres. Finally, H_2SO_4 is

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neutralized by the injection of stoichiometric amounts of ammonia, producing solid ammonium sulfate, which might be sold as fertilizer.

Here we report the results of the influences of the flue gas temperature, humidity and reaction time on the removal efficiency of SO_2, as well as mass concentration and chemical composition of the aerosols produced by pulsed corona discharge. This study was designed to investigate the aerosol formation process and to optimize operating conditions of the pulsed corona discharge to the flue gas.

2 Experiment

Fig. 1 shows a schematic diagram of the experimental setup. A high voltage pulse generator consisting of a high voltage DC source, a charging condenser and a rotary spark gap switch releases narrow pulses into the reactor. The pulsed voltage with a risetime 50—70ns, a repetition frequency 20—50 Hz, and a peak voltage 40—50 kV was recovered. The reactor is a cylinder of 56 mm inner diameter, packed with screen plate. The emitting wire is 4×4 mm in square crossection and 1200 mm in length. Typical current and voltage waveforms were recorded to calculate corona power dissipated into reactor by a HP-54503A memory oscilloscope with different probes, namely Sony model A6303, Am503s and Iwatsu model HV-p60.

In a typical experiment, the flow rate of the flue gas containing 2000 to 2100 ppmv SO_2 was about 2 Nm^3/h controlled by a rotameter. Residence times of flue gas in reactor were below 6s. The reactor and flue gas could be heated and maintained at the experimental temperature. The increase of water vapor content of flue gas was obtained through controlled injection of water into the heating tube.

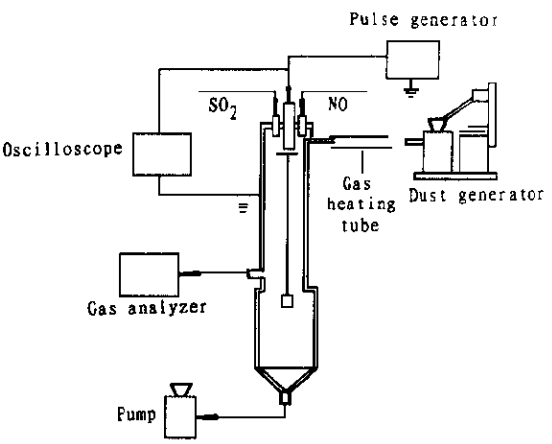

Fig. 1 Schematic diagram of the experimental setup

The SO_2 concentration after ammonia injection was measuring with a Shimadzu IRA-107 analyzer after drawing gas through a phosphoric acid scrubber. Particles formed in the pulsed corona discharge process were collected by reactor and subsequently analyzed; while the remaining soluble substances were collected in means of a distilled water filled impinger and also subsequently analyzed by ionic chromatography technique. The chemical analysis of the collected particles and of the water dissolved particles was performed to measure the content of: SO_3^{2-}, SO_4^{2-} and NH_4^+. The content of ammonium sulfates in the reaction products and collection efficiency of reactor for the particles were estimated by material balance of sulphur species.

3 Results and discussion

The direct interaction of gaseous ammonia with sulphur dioxide is known to yield ammonium sulfite under atmospheric condition, i. e. at comparatively low temperatures in the presence of water vapor. The oxidation of ammonium sulfite by oxygen to form ammonium sulfate is well known to occur at a time scale of hours in the context of atmospheric pollutants. In the dry scrubbing flue gas, the desulphurization becomes even worse, when the temperature is about 330—350K, because this is above or amidst the thermal decomposition range of ammonium sulfites.

In the pulsed corona discharge induced gas phase chemistry, however the ammonium sulfate aerosol is formed at a time scale of seconds, ammonium sulfate, the stable reaction product (the initial decomposition temperature of ammonium sulfate is about 140℃) increases the removal yield of SO_2 from flue gas. The data plotted in Fig.2 show that at a flue gas composition of 8% O_2, 10% CO_2, 9.0% H_2O, 2000 to 2100 ppmv SO_2 with balance N_2 and a gas temperature of 60 to 65℃, the percentage of ammonium sulfates in the solid reaction products increases with increasing specific energy dissipated into the reactor while injecting a stoichiometric amount of ammonia. The formation of ammonium sulfates mainly depends on the radicals of OH, HO_2, O *etc*. generated by pulsed corona discharge. Increasing the specific energy dissipated into the reactor results in high energy electrons, consequently more radicals and other excited atoms and molecules. In the pulsed corona discharge induced gas chemistry, these species chemically interact with each other and with the atoms and molecules of the gas. Especially sulfur dioxide is oxidized by these radicals and acid sulfuric, H_2SO_4, formed in presence of water vapor as following series reactions:

$$SO_2 + O \longrightarrow SO_3,$$
$$SO_2 + OH \longrightarrow HSO_3,$$
$$HSO_3 + O_2 \longrightarrow SO_3 + HO_2,$$
$$SO_2 + HO_2 \longrightarrow SO_3 + OH,$$
$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

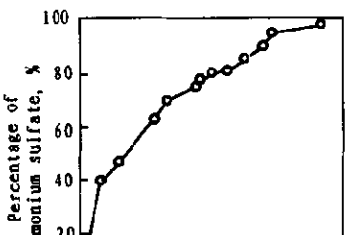

Fig.2 Percentage of ammonium sulfate in solid reaction products vs. injected energy

According to the measurements of Rodel (Rodel, 1979) and the handbook of Perry *et al*. (Perry, 1984), the vapor pressure of sulfuric acid is so small at $T = 273$—373K that the existence of gaseous sulfuric acid is negligible even in this temperature range. It is therefore reasonable for H. Matzing (Matzing, 1991) to assume that sulfuric acid nucleates prior to reaction with ammonia. Ammonium sulfate formation thus is probably not a gas-solid transition, but rather a heterogeneous reaction determined by the rate of the transport of ammonia to the surface of sulfuric acid droplets.

The data plotted in Fig.3 show that the removal yield of SO_2 from flue gas increases with increasing the specific energy

dissipated into the reactor and grows linearly in the range of the specific energy larger than 3 Wh/Nm^3. It is worth notice that the removal efficiency of SO_2 by thermal reaction is about 55%—57% and with a net increase of 0%—25% by pulsed corona discharge in the range of the specific energy 0—5 Wh/Nm^3. The removal yield of SO_2 and percentage of ammonium sulfates in reaction products shown in Fig.3 are about 80% at the specific energy 3 Wh/Nm^3. This result cannot be explained well by the mechanism of sulfur dioxide oxidation by radicals and successively formed aerosol of ammonium sulfates.

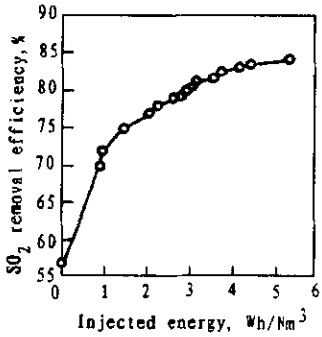

Fig.3 Efficiency of SO_2 removal vs. injected energy

The proper explanation may be based on the formation of a gaseous adduct from Lewis base NH_3 and Lewis acid SO_2, as first tentatively proposes done by Jordan (Jordan, 1988a) and Jordan *et al*. (Jordan, 1988b) for electron beam scrubbing flue gas. E. M. Hartley *et al*. (Hartley, 1975) found that the principal products of a thermo-chemical reaction were mainly $NH_3 \cdot SO_2$ and $(NH_3)_2 \cdot SO_2$ adducts in presence of water vapor:

$$NH_3(g) + SO_2(g) \longrightarrow NH_3 \cdot SO_2(g) ,$$

$$NH_3 \cdot SO_2(g) + NH_3(g) \longrightarrow (NH_3)_2 \cdot SO_2(s) .$$

Ammonium amide sulfite, $(NH_3)_2 \cdot SO_2$, further reacts with water vapor to form ammonium sulfite, $(NH_4)_2SO_3$. In pulsed corona discharge induced chemistry, due to the presence of a number of radicals, excited atoms and gas molecules of the gas, we suspect that $(NH_3)_2 \cdot SO_2$ may be oxided by O, O_3 *etc*. and form adduct, $NH_4SO_3NH_2$, on the particles' surface:

$$(NH_3)_2 \cdot SO_2(s) + O(g) \longrightarrow NH_4SO_3NH_2(s) ,$$

$$(NH_3)_2 \cdot SO_2(s) + O_3(g) \longrightarrow NH_4SO_3NH_2(s) .$$

Further reaction with water vapor forms ammonium sulfate, $(NH_4)_2SO_4$:

$$NH_4SO_3NH_2(s) + H_2O(g) \longrightarrow (NH_4)_2SO_4(s) .$$

In order to test the applicable condition, a series of experiments were made to determine the pulsed corona discharge scrubbing flue gas conditions. The influences of flue gas temperature on the chemical composition of reaction products and removal yield of SO_2 are shown in Fig.4. The percentage of ammonium sulfates in the solid products increases and the removal yield of SO_2 decreases with the increasing temperature. Due to the decrease in thermal reaction products with the decomposition of ammonium sulfites at high temperature, thus equivalently resulting in more ammonium sulfate in products, lower removal yield for SO_2. In the range of practically possible energy consumptions, i.e. the specific energy 3 Wh/Nm^3, a flue gas temperature of 60—65℃ was chosen to maintain removal efficiency of SO_2 and percentage of ammonium sulfates in solid reaction products near or above 80%, as shown in Fig.4.

Fig.5 shows the influence of the water vapor content of flue gas on the percentage of ammonium sulfates in reaction products and removal efficiency of SO_2. As expected, the removal yield of SO_2 increases with the increasing water vapor content in the flue gas, because the partial

pressure of sulfuric acid vapor is lowered with increasing pressure of water vapor and increase the rate of the gas to particle conversion. These processes, responsible for the reaction products formation, are likely to be accelerated by adsorbing of particles on water, thus resulting in more mass concentration of aerosols formed in the reactor. Meanwhile, a number of electrons are absorbed by water vapor, and more negative ions are formed in flue gas, which restrain the pulsed corona discharge through increasing ionic voltage of space. This process induces a reduction trend of the number densities of the electrons, radicals and other excited atoms and molecules produced in corona discharge process. In accordance with the data plotted in Fig.5, the percentage of ammonium sulfates in the aerosol decreases with increasing water vapor content. 9% to 11% volume of water vapor was chosen, as shown in Fig.5, to maintain the removal yield of SO_2 and the percentage of ammonium sulfates in the aerosol all at or above 80% at an energy consumption 3 Wh/Nm^3. If the water vapor content approached 14% to 15% volume, the water vapor would absorb more electrons and result in more energy consumption, while the nucleation of water vapor at the edge of reactor lead to the worse conditions of pulsed corona discharge.

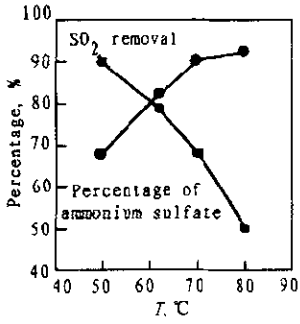

Fig.4 Effects of the flue gas temperature on SO_2 removal and reaction product conversion

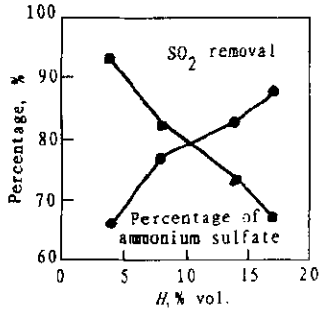

Fig.5 The effects of the flue gas humidity on SO_2 removal products conversion

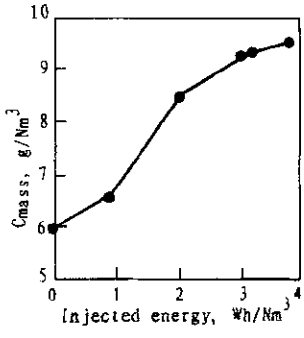

Fig.6 The mass concentration of aerosol particles formed in the reactor vs. the injected energy

In accordance with the removal yield of SO_2 from flue gas, the concentration of the aerosols formed in reactor, as shown in Fig.6, increases with the increasing specific energy. Also, the mass media diameter of the aerosol particles is smaller than 3 μm, corresponding to the measurements by Paur *et al*. (Paur, 1986). Meanwhile, the collection efficiency of these aerosols by reactor was also measured using the material balance method. The data plotted in Fig.7 show that the collection efficiency increases steeply with increasing specific energy in the range of 0.5—3 Wh/Nm^3 and become flat increase at the specific energy larger than 3 Wh/Nm^3, especially the collection efficiency of the aerosols is about 74% at the 3 Wh/Nm^3. This result indicates

that the reactor energized by pulsed power has advantages for the small particles' collection. However, for the flyash particles smaller than 3 μm, the collection efficiency of reactor is only about 40%—50% by experiments at the same operating conditions. So we suspect that the coagulation of the aerosol particles and heterogeneous reaction at the inner edge surface of reactor induced by ionics may be proper increase particle size.

Fig. 8 shows the influence of reaction time on the removal efficiency of SO_2 from flue gas. All plots are linear, and as time increases, the removal yield of SO_2 increases. At the specific energy 3 Wh/Nm^3, the plots of the removal efficiency of SO_2 vs. reaction time are linear and can be fitted with a line of slop 4.3, for the thermal reaction all plots fitted a line with a slop 2.2. All the results mean that the removal reaction rate of SO_2 in pulsed corona discharge process at 3 Wh/Nm^3 is twice faster than that of the thermal reaction.

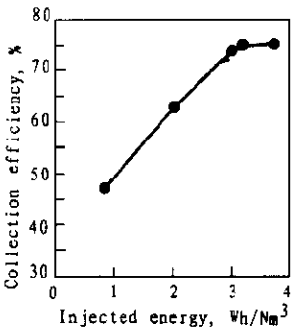

Fig. 7 The collection efficiency of aerosol particles formed in the reactor vs. the specific energy

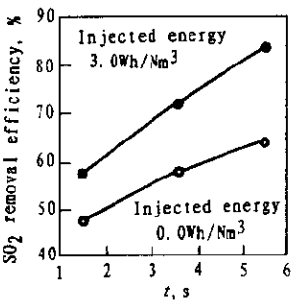

Fig. 8 The effects of reaction time on removal of SO_2

4 Conclusion

The removal of SO_2 from flue gas in the presence of ammonia is mainly dependent on the thermal reaction of SO_2 with NH_3. The net increases of SO_2 removal efficiency is about 0%—25% by pulsed corona discharge at the specific energy 0—5 Wh/Nm^3.

The mass concentration of aerosol formed in pulsed corona discharge process mainly ammonium sulfates, increases with specific energy dissipated into the reactor.

In the range of the energy consumption approachable for the application, i.e. a specific energy 3 Wh/Nm^3, the optimized operating conditions of the pulsed corona discharge to flue gas are at temperature of 60—65℃, water vapor content of 9%—11% vol. The removal efficiency of SO_2 and percentage of ammonium sulfates in the aerosols are all about or larger than 80%, the collection efficiency of reactor for the aerosols is about 74%.

The reaction rate of SO_2 removal is increased by pulsed corona discharge, and twice faster than that of the thermal reaction at the specific energy 3 Wh/Nm^3.

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