

SESSION 2C

CONTROL OF GASEOUS POLLUTANTS WITH ELECTROSTATICS

## HETEROGENOUS REACTIONS IN REMOVAL OF SO<sub>2</sub> BY CORONA DISCHARGE

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### Abstract

The SO<sub>2</sub> in the simulation gas can react with NH<sub>3</sub> even though there is no electric discharge, generating ammonium sulfite and sulfate. The lower the temperature, the higher the removal rate of SO<sub>2</sub>. This indicates that low temperature is advantageous to generation of moist salt particles, while moist particles assist SO<sub>2</sub> removal reactions in turn, manifesting the main role of the heterogenous reactions. Electric discharge not only increase the removal rate but also greatly increase the yield of hexavalent sulfur. If the test is conducted without electric discharge in advance and then corona discharge is started, the precipitated sulfite will continue to be oxidized and become sulfate. That also confirms the heterogenous reactions.

After the gas flow through the discharge region ( the reactor ), the reactions for removal of SO<sub>2</sub> still proceed in the following chambers. Moreover, the oxidation rate is remarkably higher than that with no discharge. That shows that the activated particles continue playing a catalytic role when they flow into the precipitation chambers. Rough estimation gives a life time longer than 30s of the activated particles. It is these activated particles which further the oxidation of the precipitated sulfite.

Whether there is or not electric discharge, the decrease rule of the concentration of SO<sub>2</sub> in the gas flow is slower than exponential law. The oxidation rate is also getting down along with the gas flow. The time constant of decrease of the concentration of SO<sub>2</sub> is inversely correlated with its concentration.

### Background

Study on kinetics in gas (homogeneous) phase for removal of SO<sub>2</sub> & NO<sub>x</sub> by non-thermal plasma has lasted for more than 20 years. In 1991, H. Matzing [1] presented the most detailed analysis on the kinetic processes of removal of SO<sub>2</sub> & NO<sub>x</sub> by E-beam. The oxidation of SO<sub>2</sub> seems not due to some chain process, but seems mainly due to consumption of one hydroxyl radical OH for oxidation of each SO<sub>2</sub> molecule. Under the conditions of E-beam process, the yield of OH (the number of generated OH by injection of 1heV energy, i.e. G(OH) value) is G(OH)=6.5 molec./heV. In gas discharge, G(OH) is only a fraction of unit [2], say less than 0.9 as estimated. The energy efficiency for removal of SO<sub>2</sub> can be expressed as G(-SO<sub>2</sub>), which is the number of removed SO<sub>2</sub> molecules per heV. For E-beam, G(-SO<sub>2</sub>)= 6.7 molec./heV = 161mg(SO<sub>2</sub>)/wh, while for gas discharge G(-SO<sub>2</sub>) = 0.9molec./heV = 21 mg/wh. That is true if the gas with SO<sub>2</sub> is at low humidity ( P<sub>H<sub>2</sub>O</sub> < 8kPa ≈ 60mmHg) and high temperature. [3] To break up the bond of H<sub>2</sub>O and generate a hydroxyl radical OH (and an atom H), 5.2eV is needed. Speaking at most, even though the one heV injected energy were totally used for generation of OH radicals, G(OH) would be only G(OH)=19.2 molec./heV=461mg/wh.

However, if the humidity is high and even ammonia is injected, the experimental results are rather different. A. Mizuno [4] obtained a result of  $G(-SO_2)=10$  molec./heV= 240 mg/wh for E-beam treatment with a  $SO_2$  removal efficiency of 92% at a temperature 22°C and R.H.100%. Under the same conditions, he got  $G(-SO_2) = 40$  molec./heV= 960 mg/wh when the nonthermal plasma is injected by gas discharge. It is generally considered that in this case, oxidation of  $SO_2$  proceeds in the droplets formed in the gas. Furthermore  $SO_2$  removal reactions strongly depends upon the temperature of the gas. Under the conditions of a fixed humidity and a constant injection of energy, with rise of gas temperature, the energy efficiency gradually decreases until it reaches some constant [3]. Kinetics in homogenous phase can not explain this property.

Paur et al [4] pointed that with a constant dose of E-beam injection and constant ammonia injection, the regulation for the yield of sulfate against the humidity manifests two mechanisms. When R.H.is lower than 20%, the reactions appears to mainly proceed in gas phase, while R.H. is higher than 20%, the sulfate increases linearly both with the humidity, which shows a mechanism of heterogenous phase reactions, and with the ammonia stoichiometry. That shows that the activated oxidation in the heterogenous phase is positively correlated with the PH value in the heterogenous phase. Jordan [5] indicated that about 70-90% sulfur removal reactions occur in surfaces and the filter cake, hinting the domination of the heterogenous  $SO_2$  removal reactions. In fact, under some circumstances, with injection of ammonia into the gas containing  $SO_2$ , most part of the  $SO_2$  can be removed without any energy injection, the removal rate and the composition of the powder product depending upon temperature, humidity, stoichiometry and reaction time [6] [7].

Nevertheless, what the functions of the plasma-activated heterogenous reactions need to be explained by further experimental results.

Our experimental results suggest that the electric discharge plays a role to increase both removal rate and oxidation rate of  $SO_2$ . The reactions manifest domination of heterogenous mechanism.

### Experimental Setup

The gas flow rate in the experimental system is 0.4Nm<sup>3</sup>/h. Air mixed with  $SO_2$  and adjusted with moisture in the mixing chamber is sent to the plasma reactor. The ammonia diluted with nitrogen and heated to preset temperature is injected to the reactor in parallel. The precipitation chambers of 1st, 2nd and 3rd stages are connected after the reactor in the order. After passing through the three precipitation chambers, the test gas flows to wash bottles to wash out the residual ammonia with phosphorous acid, and is then sampled for the measurement of  $SO_2$  and discharged out of the test system as end gas. The parts of the system from the entrance of the mixing chamber to the  $SO_2$  sampling point are placed in a constant temperature box, which can be adjusted from room temperature to 100°C. The concentration of  $SO_2$  is measured with type-40 chemi-fluorescent analyser, calibrated by iodine titration. The initial concentration of  $SO_2$  is measured when ammonia has not been injected. The content of  $SO_4^{2-}$  is measured with a DMR-22 spectrophotometer and the content of  $SO_3^{2-}$  is measured by iodine titration.

The streamer discharge is generated by a voltage of peak + 40kV superimposed on a bias of +20kV. The injected power is kept constant. The parameters of the circuit is also fixed so as to have a steady waveforms. The initial  $SO_2$  concentration is set at about 2000ppmv, and ammonia 3500ppmv. Humidity of the gas is 11.3 vol%. This test aims at observing

corona discharge-activated oxidation of tetravalent sulfur compounds through relative comparison between the deposit within the gas discharge and that with no electric discharge treatment.

### Experimental Results

The treating time of the gas in the reactor is its residence time  $\tau_0$ .  $\tau_0$  = reactor volume/flow rate. The residence times in the 1st, 2nd and 3rd precipitation chambers are also computed in this way. The reactor can be looked at as the 0th precipitation chamber. Let  $S_i(V)$  ( $i=0,1,2, 3$ ) express the mass of  $SO_2$  consumed for its conversion into hexavalent sulfur under the action of electric discharge in the  $i$ th chamber;  $S(V)=S_0(V) + S_1(V) + S_2(V) + S_3(V) + S_4(V)$ ;  $S_i(IV)$  and  $S(IV)$  express the tetravalent case.  $\xi_i(IV)=S_i(IV)/ (S(IV)+S(V))$  and  $\xi(IV)=S(IV)/ (S(IV)+S(V))$  be the relative deposit for hexavalent sulfur for the  $i$ th chamber and the whole system respectively. We express the quantities related to no electric discharge action by \*, such as  $S_i^*(V)$ ,  $S^*(V)$ ,  $\xi_i^*(V)$  and  $\xi^*(V)$ . Table 1 specifies the relative precipitation rate  $\xi_i$  ( electric discharge ) and  $\xi_i^*$  ( no discharge ) and  $\xi_i/\tau_i$ ,  $\xi_i^*/\tau_i$ . In fig.2,  $\xi = S(V)/ (S(IV)+S(V))$ ;  $\xi^*=S^*(V)/ (S^*(IV)+S^*(V))$  show the relative yields of hexavalent sulfur in the whole system. In Fig.2,  $\eta SO_2$  and  $\eta SO_2^*$  express the removal rates for the cases of there being discharge and no discharge respectively. The main results are given as follows.

(1) It can be found from Fig.2 that under the conditions of this experiment, the  $SO_2$  in the simulation gas can react with  $NH_3$  even though there is no electric discharge, generating ammonium sulfite and sulfate. The lower the temperature, the higher the removal rate of  $SO_2$ . This indicates that low temperature is advantageous to generation of moist salt particles, while moist particles assist  $SO_2$  removal reactions in turn, manifesting the main role of the heterogenous reactions.

(2) Fig.2 shows that electric discharge not only increase the removal rate but also greatly increase the yield of hexavalent sulfur. For example at  $55^\circ C$ , electric discharge increases the  $SO_2$  consumed for its conversion into hexavalent sulfur from about 20% to more than 90%. If the test is conducted without electric discharge in advance and then corona discharge is started, the precipitated sulfite will continue to be oxidized and become sulfate, which can be seen from Fig.2 or Table 1. That also confirms the heterogenous reactions.

(3) It can be found from Table 1, that after the gas flow out of the discharge region ( the reactor ), the reactions for removal of  $SO_2$  still proceed in the following chambers. Moreover, the oxidation rate is remarkably higher than that with no discharge. That shows that the activated particles continue playing a catalytic role when they flow into the precipitation chambers. Rough estimation gives a life time longer than 30s of the activated particles. It is these activated particles which further the oxidation of the precipitated sulfite.

In the experiment at  $55^\circ C$  with discharge in the reactor,  $\xi_1/\tau_1 = 3.65\%/s$  in the 1st chamber, which is greater than  $\xi_0/\tau_0 = 2.55\%/s$  in the reactor. That indicates that the generation rate of hexavalent sulfur in the 1st chamber is higher than in the reactor under the experimental conditions. That seems that the active oxygen is carried by droplets or moist solid particles. Under the conditions of no discharge, a part of tetravalent deposited material also be oxidized to hexavalence, but the oxidation rate in every chamber is lower than the case of there being discharge.

(4) Whether there is or not electric discharge, the decrease rule of

the concentration of SO<sub>2</sub> in the gas flow is slower than exponential law. The oxidation rate is also getting down along with the gas flow. The time constant of decrease of the concentration of SO<sub>2</sub> is inversely correlated with its concentration.

### Discussion

- (1) Under the conditions of existence of ammonia and water vapor, the sulfur dioxide can be partly removed in tens seconds without action of electric discharge, generating deposit, if the concentration of SO<sub>2</sub> is high enough. When the gas is treated with discharge, the reaction becomes faster and the oxidation rate is also increased. However, gas reaction kinetics can not explain the energy efficiency obtained in SO<sub>2</sub> removal experiments and still can not give reasons on the results obtained in the tests without discharge. Therefore it is necessary to adopt the chain process theory to explain the spontaneous reaction of SO<sub>2</sub>. There are chain processes in solution for the oxidation of tetravalent sulfur through the propagations of the radicals of SO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup> and SO<sub>5</sub><sup>-</sup> [8]. Benner (8) experimentally proved that under the conditions of existence of ammonia, SO<sub>2</sub> can be oxidized to SO<sub>4</sub><sup>-</sup> in water film, generating (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. At room temperature and 60% relative humidity, inversion of 81% of SO<sub>2</sub> into (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is observed. Benner considered that the wall of the vessels provides places where the reactions may occur. However the surfaces of the product (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> can also help oxidation of SO<sub>2</sub>. In fact, ammonium sulfite is very soluble. At high humidity, it deliquesces. As a result, the generated salt particles are covered with a thin layer of sulfite solution. Just in this film, the tetravalent sulfur is oxidized through a series of chain propagations. To make full use of the chain processes, the limiting factors, chain destructions should be controlled.
- (2) As stated above, gas discharge injects active particles to make the oxidation of SO<sub>2</sub> faster. Therefore, to increase the energy efficiency, optimisation of the initial condition of discharge of great importance. High peak voltage and high rise rate of voltage is helpful because the primary streamer occupies a large portion in this case, generating high energy electrons with relatively small amount injected energy. High energy electrons excite radicals.

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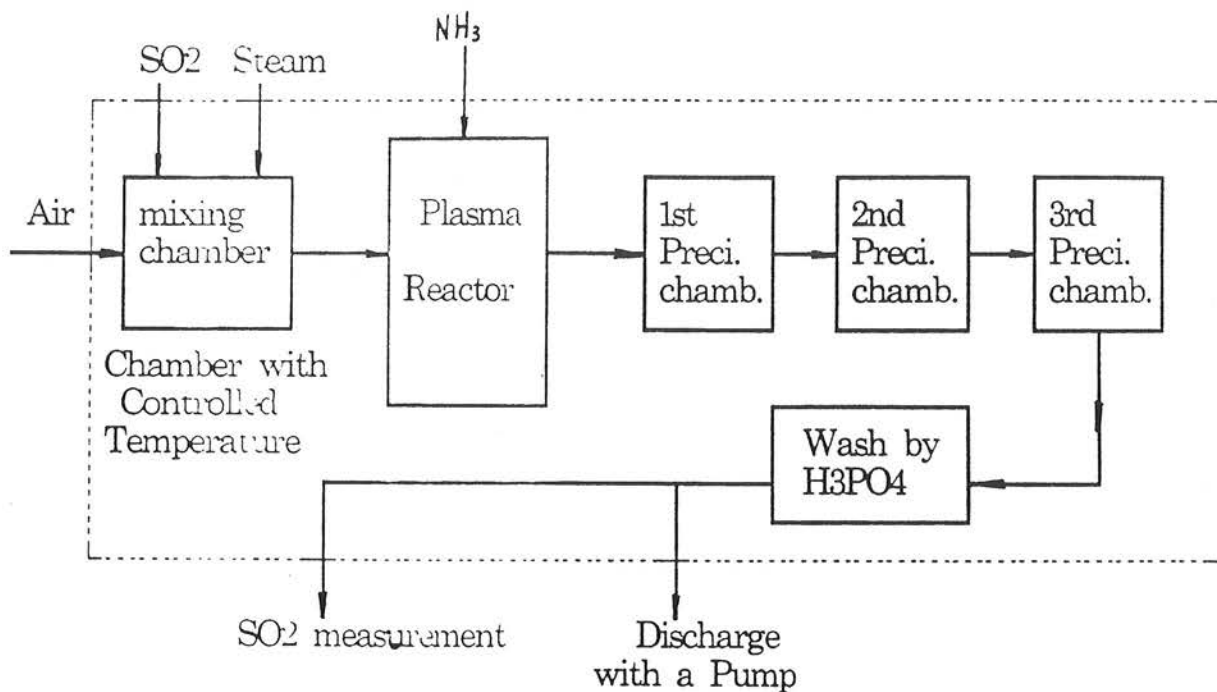


Fig. 1 Schematic of the experimental setup

- \* Flow Rate ————— 0.4Nm<sup>3</sup>/h
- \* Ammonia injected separately
- \* Peak Voltage  $V_p=40\text{kV} + \text{Bias } 20\text{kV}$
- \* Cylindrical Pulse Discharge Reactor with Concentric Wire
- \* Three Precipitation Chambers Following the Reactor in Series
- \* Humidity of the Gas ————— 11.4 Vol.%
- \* Constant Temperature ————— Room to 100°C

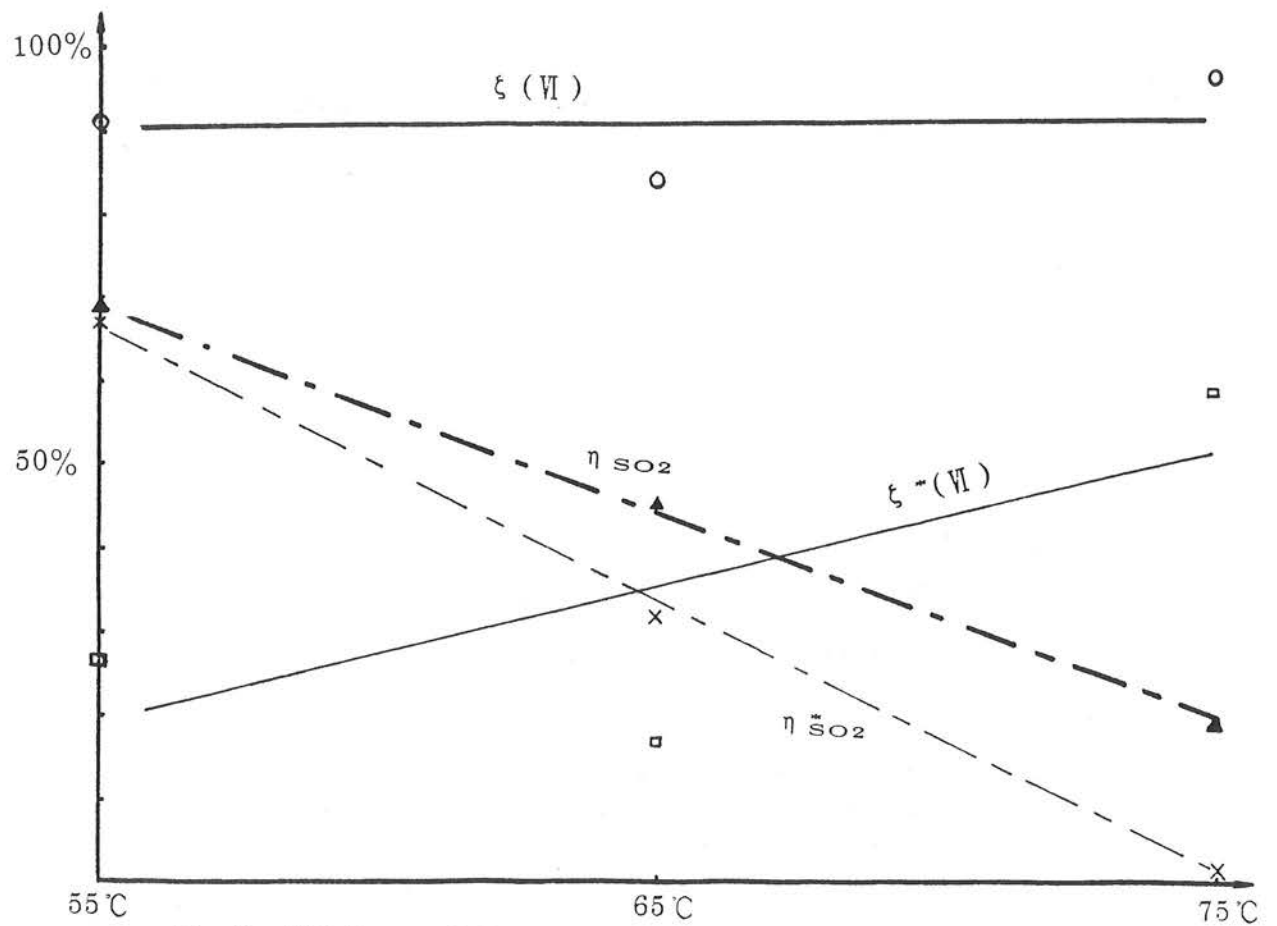


Fig. 2 SO<sub>2</sub> Removal Rate  $\eta_{SO_2}$  and  $\eta_{\dot{S}O_2}$  against Temperature

Table 1 Relative Comparison of the yields of sulfate and sulfite in different chambers and at different temperatures

$S_i(VI)$  ( $i=0,1,2,3$ ):  $SO_2$  (in gram) consumed for generation of the sulfate in the reactor ( $i=0$ ) and the 1st, 2nd and 3rd precipitation chamber with the action of corona discharge.

$$S(VI) = S_0(VI) + S_1(VI) + S_2(VI) + S_3(VI) + S_4(VI).$$

$S_i(IV)$  and  $S(IV)$  are for the tetravalent case.

$$\xi_i(VI) = S_i(VI) / (S(IV) + S(VI)), \quad \xi_i(IV) = S_i(IV) / (S(IV) + S(VI))$$

$S_{i*}$  and  $\xi_{i*}$  are for the case of no corona discharge.

$\tau_i$  is the resident time in the  $i$ th chamber.

t °C	Relative Parameters %	Electric Corona	Reactor	1st Chamber	2nd Chamber	3rd Chamber	4th Chamber
55	$\frac{S_i(VI)}{S(VI) + S(IV)} =$	Yes	57.17	29.35	2.81	0.959	0.693
	$\xi_i(VI) / \tau_i$		2.55	3.65	1.94	0.82	0.54
	$\frac{S_i(IV)}{S(VI) + S(IV)} =$	Yes	3.7	4.79	0.225	0.156	0.114
	$\xi_i(IV) / \tau_i$		0.166	0.596	0.156	0.134	0.089
	$\frac{S_{i*}(VI)}{S*(VI) + S*(IV)} =$	No	23.3	1.95	1.01	0.174	0.124
	$\xi_{i*}(VI) / \tau_i$		1.04	0.243	0.697	0.148	0.096
	$\frac{S_{i*}(IV)}{S*(VI) + S*(IV)} =$	No	70.83	1.86	0.219	0.107	0.406
	$\xi_{i*}(IV) / \tau_i$		3.16	0.231	0.151	.091	0.315



Table 1 Relative Comparison of the yields of sulfate and sulfite in different chambers and at different temperatures

$S_i(W)$  ( $i=0,1,2,3$ ):  $SO_2$  (in gram) consumed for generation of the sulfate in the reactor ( $i=0$ ) and the 1st, 2nd and 3rd precipitation chamber with the action of corona discharge.

$$S(W) = S_0(W) + S_1(W) + S_2(W) + S_3(W) + S_4(W).$$

$S_i(N)$  and  $S(N)$  are for the tetravalent case.

$$\xi_i(W) = S_i(W) / (S(N) + S(W)), \quad \xi_i(N) = S_i(N) / (S(N) + S(W))$$

$S_i^*$  and  $\xi_i^*$  are for the case of no corona discharge.

$\tau_i$  is the resident time in the  $i$ th chamber.

65	$\frac{S_i(W)}{S(W)+S(N)} =$	Yes	73.0	13.0	0.665	0.665	0.056
	$\xi_i(W) / \tau_i$		3.25	1.62	0.046	0.057	0.005
	$\frac{S_i(N)}{S(W)+S(N)} =$	Yes	11.8	0.682	0.125	0.037	0.017
	$\xi_i(N) / \tau_i$		0.525	0.085	0.086	0.031	0.013
	$\frac{S_i^*(W)}{S^*(W)+S^*(N)} =$	No	13.33	2.04	0.355	0.286	0.286
	$\xi_i^*(W) / \tau_i$		0.595	0.025	0.245	0.245	0.223
75	$\frac{S_i(W)}{S(W)-S(N)} =$	Yes	89.32	6.39	0.438	0.438	0.038
	$\xi_i(W) / \tau_i$		3.99	0.795	0.303	0.376	0.030
	$\frac{S_i(N)}{S(W)-S(N)} =$	Yes	2.68	0.434	0.159	0.051	0.045
	$\xi_i(N) / \tau_i$		0.120	0.254	0.110	0.044	0.035
	$\frac{S_i^*(W)}{S^*(W)+S^*(N)} =$	No	39.40	5.70	5.90		5.36
	$\xi_i^*(W) / \tau_i$		1.76	0.710	4.03		4.56
	$\frac{S_i^*(N)}{S^*(W)+S^*(N)} =$	No	21.30	1.74	0.883		1.84
	$\xi_i^*(N) / \tau_i$		0.952	0.217	0.610		1.44