Influence of Oxygen and Water Vapor on Removal of Sulfur Compounds by Electron Attachment

Hajime Tamon, Noriaki Sano, and Morio Okazaki
Dept. of Chemical Engineering, Kyoto University, Kyoto 606-01, Japan

When an electron collides with a gas molecule, a negative ion is produced in a probability depending on the electron energy, the structure of the gas molecule, and its electron affinity (Massey, 1976, 1979; Caledonia, 1975). This reaction is called electron attachment. In previous articles, a novel gas purification method based on the high selectivity of electron attachment reaction has been proposed (Tamon et al., 1989, 1995). In the proposed gas-purification principle, the gas impurities are ionized by colliding with electrons that are produced in a corona discharge between a wire cathode and a cylindrical anode. The negative ions formed by electron attachment drift to the anode. On the basis of removing the negative ions at the anode, two types of reactors, deposition-type reactor and sweep-out-type reactor, have been proposed. The authors have then conducted the removals of seven kinds of sulfur compounds [SF_6, H_2S, CH_3SH, $(CH_3)_2S$, CS_2, COS and SO_2] by the deposition-type reactor and dilute iodine and oxygen by the sweep-out-type reactor from nitrogen (Tamon et al., 1995).

Since oxygen and water vapor coexist in the actual process, it is necessary to examine their influence on the removal efficiency for the practical application. In this article, we study experimentally the influence of coexisting oxygen and water vapor on the removal of six sulfur compounds [H_2S, CH_3SH, $(CH_3)_2S$, CS_2, COS, and SO_2] by use of the deposition-type reactor. We also discuss the removal mechanism of the sulfur compounds in air by electron attachment.

Experimental Studies

Figure 1 shows the experimental apparatus. The deposition-type reactor (Tamon et al., 1995) consists of a 38-mm-ID, 280-mm-long cylindrical anode (brass pipe) and a 0.3-mm-dia. wire cathode to generate corona discharge. The cathode is sustained by a ceramic insulator on the top and by Teflon threads on the bottom. The wall of the reactor is acrylic except for the electrode. To generate the discharge current of 0.1 ~ 1.5 mA, the cathode is charged with high direct voltage, and the anode is earthed. The voltage applied on the cathode is $-3.5 \sim -8.7$ kV in the absence of oxygen, or $-6 \sim -15$ kV in the presence of oxygen. Electron energy in the corona discharge is estimated above 0.3 eV, which is higher in close positions to the cathode than in areas around the anode because of the electric field profile inside the reactor (Tamon et al., 1995).

The concentrations of sulfur compounds and coexisting oxygen are adjusted by mixing standard gases with nitrogen. The concentration of water vapor is controlled by bubbling of inert gas (N_2) in distilled water in a temperature-controlled bath. The inlet concentration of sulfur compounds (C_{in}), oxygen (C_{O_2}), and water vapor (C_{H_2O}) are respectively 29 ~ 122 ppm, 0 ~ 49%, and 300 ~ 13,000 ppm. Sulfur compounds, oxygen, and water vapor are analyzed respectively by a FPD gas chromatograph (Shimadzu Corporation, GC-7A), a zirconia-type oxygen analyzer (Toray Industries Inc., LC700), and a dew point hygrometer (Yokogawa Electric Corporation, MODEL 2586). A gas chromatograph mass spectrometer (GCMS) (Shimadzu Corporation, MS-QP1000S) is used to identify reaction byproducts of electron attachment. The GCMS is equipped with the same GC column (1.2.3 Tris [2-(Cyanoethoxy)] Propane 25% on Shimalite) as the FPD gas chromatograph.

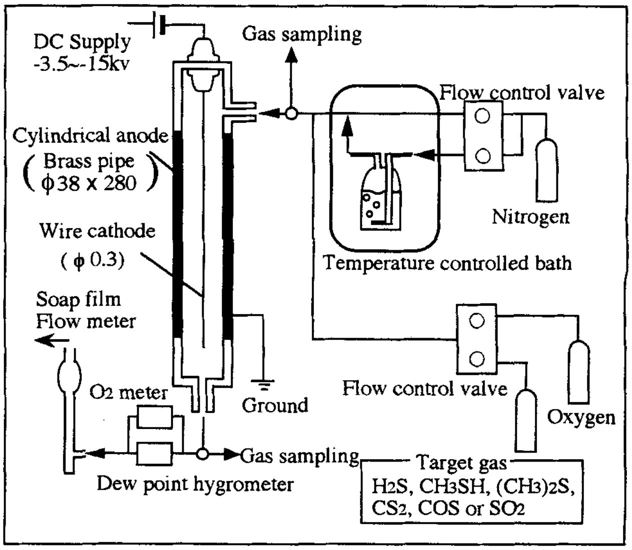
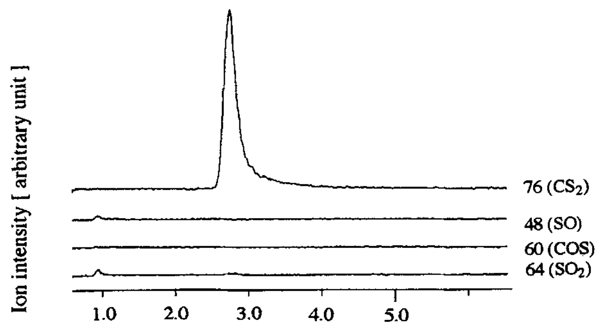
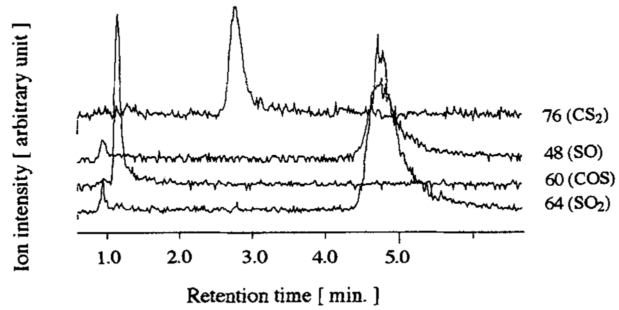


Figure 1. Experimental apparatus.



(a) Analysis of inlet gas by GCMS



(b) Analysis of outlet gas by GCMS

Figure 2. GCMS spectra in CS_2 removal from N_2-O_2 mixture.

$C_{in} = 82.1$ ppm; $I = 0.2$ mA; $SV = 18.9\ h^{-1}$; $C_{O_2} = 1.0\%$.

Results and Discussion

Effect of coexisting oxygen

It is necessary to define a criterion to evaluate removal efficiency. We define the efficiency as Eq. 1 concerning the removal of sulfur atoms constituting the sulfur compounds.

$$\psi = 1 - \frac{C_{out} + kC_{sub}}{C_{in}} \tag{1}$$

Here, ψ is the removal efficiency, C_{out} (ppm) and C_{in} (ppm) are the outlet and inlet concentrations of a sulfur compound, and C_{sub} (ppm) is the concentration of reaction byproducts in the outlet gas. k is zero when no reaction byproduct appears. When the byproducts appear, k is 1/2 for the removal of CS_2, or 1 for other removals from the stoichiometric relation if a molecule of the reaction byproducts contains one sulfur atom.

It is important to observe the reaction byproducts because the formation of the reaction byproducts which contain sulfur causes the decrease of the removal efficiency. Figure 2 is one example of GCMS spectra that shows the formation of SO_2 and COS from CS_2. Mass numbers of CS_2, SO, COS, and SO_2 are respectively 76, 48, 60, and 64. Comparison between Figures 2a and 2b shows disappearance of CS_2 and appearance of COS and SO_2. SO here is considered as a fragment from SO_2 in the GCMS.

Table 1 shows the influence of coexisting oxygen on the formation of reaction byproducts and the removal efficiency. It also shows the experimental conditions, dependencies of the byproducts formations and removal efficiencies ψ on the discharge current I and the concentration of oxygen C_{O_2}. φ_{sub} is the conversion of a reacted sulfur compound into a reaction byproduct, a ratio of the formation of a reaction byproduct to the removal of a target gas. It is calculated based on quantity of sulfur atoms as Eq. 2.

$$\varphi_{sub} = \frac{kC_{sub}}{C_{in} - C_{out}} \quad (k \text{ is } 1/2 \text{ for the removal of } CS_2 \text{ or } 1 \text{ for other removals}) \tag{2}$$

Though SO_2 is produced in the removals of CS_2, COS, and CH_3SH, it becomes negligible when the discharge current is high. The formation of SO_2 decreases as concentra-

Table 1. Influence of Coexisting Oxygen on Reaction Byproducts and Removal Efficiency

	Conditions				Byproducts Formation				Removal Efficiency		
							Change of φ_{sub}			Change of ψ	
Target Gas	I, mA (V, kV)	SV h^{-1}	C_{O_2} %	C_{in} ppm	Byproducts	φ_{sub}	I	C_{O_2}	ψ_{max}[†]	I	C_{O_2}
SO_2	0.25 ~ 1.5 (10.1 ~ 14.5)	18.9	0 ~ 18	101	none	0	—	—	0.95	incr.[‡]	incr.[‡]
CS_2	0.18 ~ 1.5 (9.3 ~ 14.8)	18.9	0 ~ 49	30	SO_2 COS	trace* 0.3 ~ 0.05	decr.** decr.	decr.** incr.	0.98	incr.	max. at 2%[‡]
COS	0.2 ~ 1.5 (9.5 ~ 14.8)	18.9	0 ~ 50	29	SO_2	neglig.	—	—	0.92	incr.	max. at 2%
CH_3SH	0.05 ~ 1.0 (6.3 ~ 14.9)	18.9	0 ~ 20	69	SO_2 H_2S or COS	trace* neglig.	decr. —	decr. —	1.0	incr.	incr.
$(CH_3)_2S$	0.25 ~ 1.0 (6.0 ~ 10)	18.9	0 ~ 22	70	none	0	—	—	1.0	incr.	incr.

*When the concentration of oxygen for CS_2 is more than 5%, φ_{sub} is negligible with high discharge current (> 0.5 mA); when that for CH_3SH is more than 3.5%, φ_{sub} is negligible with high discharge current (> 0.2 mA).

**φ_{sub} for I decreases with the discharge current; φ_{sub} for C_{O_2} decreases with the concentration of oxygen.

[†] Maximum ψ under the experimental condition.

[‡] ψ for I increases with the discharge current; ψ of SO_2 increases with the concentration of oxygen; and ψ of CS_2 becomes maximum at 2% of concentration of oxygen.

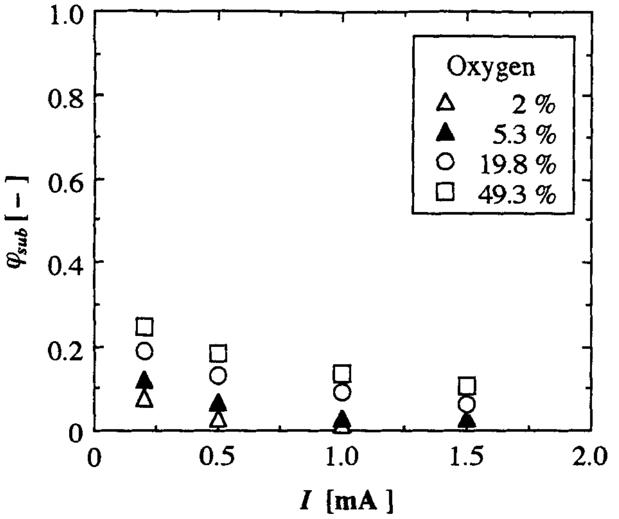


Figure 3. COS produced in CS_2 removal from N_2-O_2 mixtures.

$C_{in} = 29.8$ ppm; $SV = 18.9\ h^{-1}$.

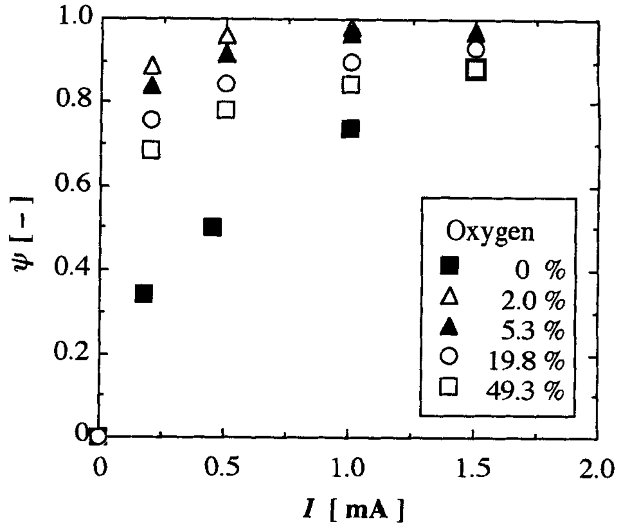


Figure 4. Removal efficiency of CS_2 in presence of O_2.

$C_{in} = 29.8$ ppm; $SV = 18.9\ h^{-1}$.

tion of oxygen increases. Also, COS is formed in the removal of CS_2 and it decreases with the discharge current. However, the formation of COS increases as O_2 concentration increases, resulting in the excess concentration of oxygen that causes the decrease of the removal efficiencies of CS_2 and COS. Other removals show the increase of the removal efficiency with the concentration of oxygen. The removal efficiencies for all sulfur compounds increase with the discharge current and reach the very high removal efficiencies. Conclusively, it is found that the removal efficiencies of these sulfur compounds are greatly improved by mixing oxygen in the inlet gas.

Figure 3 shows the formation of COS in the removal of CS_2. Figure 4 shows the removals of CS_2 with several concentrations of oxygen. It is obvious that the removal efficiency is greatly improved by mixture of oxygen. Also, it can be seen that there is an optimum concentration of oxygen for the maximum removal efficiency of CS_2. This optimum oxygen concentration appears because of the formation of the byproduct, COS.

Effect of coexisting water vapor

Table 2 summarizes the influence of coexisting water vapor on the formation of reaction byproducts and the removal efficiency in the same way as Table 1. Here, the dependencies of the byproducts formations and the removal efficiencies ψ on the discharge current I and the concentration of water vapor C_{H_2O} are shown.

The reaction byproduct produced in the removals of CS_2, COS, CH_3SH, and $(CH_3)_2S$ is SO_2. The formation of SO_2 increases with the discharge current and this tendency negatively influences the removal efficiencies. COS is produced in the removal of CS_2, as well as one with coexisting oxygen. The removals here do not reach high removal efficiencies except for H_2S. That is because the formation of SO_2 of the reaction byproduct is significant especially in the high discharge current range. In the removal of CH_3SH and $(CH_3)_2S$, the formation of SO_2 is so much that there are optimum discharge currents to show the maximum removal efficiencies. Nevertheless, in the low discharge current range, the removal efficiencies are improved by mixing water vapor in the inlet gas.

Table 2. Influence of Coexisting Water Vapor on Reaction Byproducts and Removal Efficiency

	Conditions				Byproducts Formation				Removal Efficiency		
							Change of φ_{sub}			Change of ψ	
Target Gas	I, mA (V, kV)	SV h^{-1}	C_{H_2O} ppm	C_{in} ppm	Byproducts	φ_{sub}	I	C_{H_2O}	ψ_{max}	I	C_{H_2O}
H_2S	0.2 ~ 1.45 (3.5 ~ 8.7)	37.8	400 ~ 11,000	60	none	0	—	—	1.0	incr.	incr.
SO_2	0.25 ~ 1.5 (4.5 ~ 5.7)	37.8	400 ~ 13,000	122	none	0	—	—	0.39	incr.	incr.
CS_2	0.25 ~ 1.4 (4.9 ~ 7.5)	37.8	300 ~ 11,000	48	SO_2 COS	0.1 ~ 0.35 0.5 ~ 0.15	incr. decr.	decr. incr.	0.66	incr.	incr.
COS	0.25 ~ 1.5 (4.5 ~ 5.7)	37.8	650 ~ 10,000	53	SO_2	0 ~ 0.35	incr.	decr.	0.64	incr.	incr.
CH_3SH	0.1 ~ 1.5 (4.8 ~ 6.5)	37.8	1,000 ~ 10,000	40	SO_2	0.2 ~ 0.55	incr.	incr.	0.65	max. at 0.25 ~ 0.5 mA	incr.
$(CH_3)_2S$	0.25 ~ 1.5 (4.5 ~ 5.6)	52.9	1,100 ~ 9,100	38	SO_2	0.5 ~ 0.7	incr.	incr.	0.27	max. at 0.5 mA	incr.

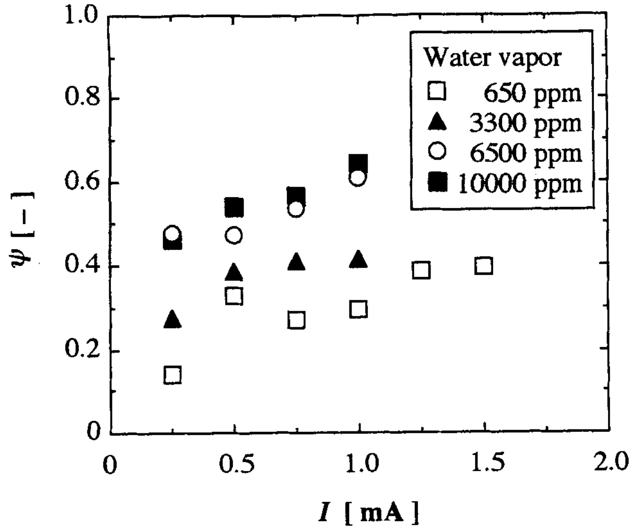


Figure 5. Removal efficiency of COS in presence of H_2O.

C_{in} = 52.8 ppm; SV = 37.8 h^{-1}.

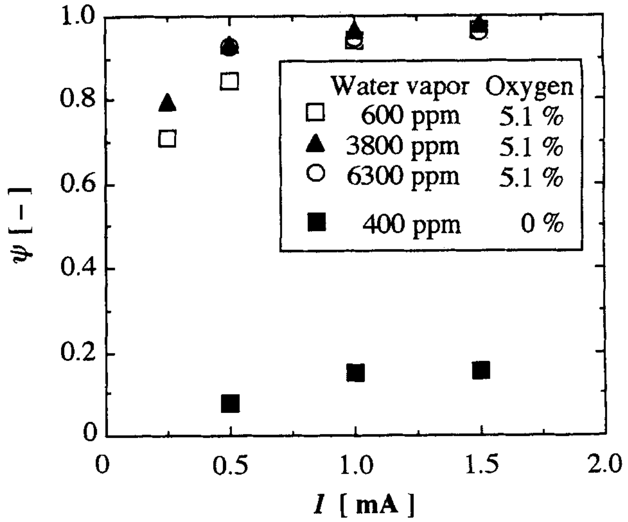


Figure 6. Removal efficiency of SO_2 in presence of O_2 and H_2O.

C_{in} = 120.0 ppm; SV = 37.8 h^{-1}.

The typical result of the removal experiment in the presence of water vapor is shown in Figure 5. This figure shows the removal efficiency of SO_2 against the discharge current with several concentrations of water vapor. The increase of the removal efficiencies with the discharge current reflects the increase of the collisions of electrons with gas molecules. As for the influence of water vapor, the removal efficiency is increased by mixture of water vapor.

Effect of coexisting oxygen and water vapor

Furthermore, we have examined the influence of the simultaneous mixture of oxygen and water vapor in gas on the removal efficiency. The results are summarized in Table 3. It shows the influence of the concentration of water vapor on the formation of reaction byproducts and the removal efficiency with a certain concentration of oxygen.

Though the formation of the reaction byproducts SO_2 and COS is observed, it decreases with the discharge current. The removal efficiencies increase with the discharge current and these removals show very high removal efficiencies at high discharge current range. The above tendencies are the same as the ones in the removals from N_2-O_2 mixtures. In the low discharge current range, the removal efficiencies of SO_2 and $(CH_3)_2S$ increase with the concentration of water vapor. This tendency is consistent with the removals from nitrogen-water vapor mixtures. On the other hand, the removal of CS_2 shows the opposite tendency though the influence of concentration of water vapor is negligible in the high discharge current range. This is because of the formation of the byproduct COS.

Figure 6 shows the removal efficiency of SO_2 with 5.1% oxygen and 600 ~ 6,300 ppm water vapor. Also, this figure shows the removal efficiency without oxygen with 400 ppm water vapor for comparison. This result shows very high removal efficiency in the high discharge current range in the presence of oxygen. In the low discharge current range, sufficient mixture of water vapor raises the removal efficiency. The influence of concentration of water vapor on the removal efficiency is negligible in the high discharge current range.

Conclusively, under this experimental condition, the removal efficiencies in the presence of oxygen and water vapor become very high compared with ones without coexisting oxygen and water vapor. These results suggest that the proposed gas purification method is applicable for the removal of sulfur compounds from air.

Removal mechanism

When there are coexisting gases, they will react with electrons. Electron attachment to oxygen was reported in the lit-

Table 3. Influence of Coexisting Water Vapor on Removal Efficiency in Presence of Oxygen and Byproducts Formation

	Conditions					Byproducts Formation				Removal Efficiency		
								Change of φ_{sub}			Change of ψ	
Target Gas	I, mA (V, kV)	SV h^{-1}	C_{O_2} %	C_{H_2O} ppm	C_{in} ppm	Byproducts	φ_{sub}	I	C_{H_2O}	ψ_{max}	I	C_{H_2O}
SO_2	0.25 ~ 1.5 (9.0 ~ 14.5)	37.8	5.0	600 ~ 6,300	120	none	0	—	—	0.98	incr.	incr.*
CS_2	0.25 ~ 1.5 (8.5 ~ 14.0)	37.8	14.5	600 ~ 9,500	65	SO_2 COS	0.01 ~ 0.12 0.04 ~ 0.14	decr. decr.	neglig. incr.	0.93	incr.	decr.*
$(CH_3)_2S$	0.1 ~ 1.5 (8.0 ~ 14.0)	52.9	7.9	600 ~ 5,600	39	SO_2	0.00 ~ 0.22	decr.	neglig.	0.98	incr.	incr.*

*Negligible in high discharge current range.

erature (Moruzzi and Phelps, 1966; Massey, 1976; Rapp and Briglia, 1965; Chantry and Schulz, 1967).

$$O_2 + e^- \rightarrow O_2^- \tag{3}$$

$$O_2 + e^- \rightarrow O + O^- \tag{4}$$

Moruzzi and Phelps (1966) observed that the reaction of Eq. 3 occurred in low electron energy range ($E/p < 1.5\ \mathrm{V \cdot m^{-1} \cdot Pa^{-1}}$). The reaction of Eq. 4 occurred in the higher electron energy range. In the presence of water vapor, H^-, O^-, OH^- would be produced from the dissociative electron attachment to H_2O (Moruzzi and Phelps, 1966; Massey, 1976; Schulz, 1960; Compton and Christophorou, 1967; Dorman, 1966). Those reactions consume electrons and decrease the collisions of electrons to sulfur compound molecules. Nevertheless, the experimental results have shown that the removal efficiency of sulfur compounds is greatly increased by mixture of oxygen and water vapor.

To evaluate the removal efficiency, it is convenient to calculate the mean number of gas molecules removed by one electron as Eq. 5

$$n_e = N_r / N_{e0} \tag{5}$$

Here n_e is the mean number of the sulfur compound molecules removed by one electron. N_r is the number of removed gas molecules per unit time, and N_{e0} is the number of electrons that appeared in the corona discharge per unit time. To show the typical example, we tabulate n_e in Table 4 for the removal of SO_2 in the presence of water vapor (3,700 ppm) and in the presence of both water vapor (3,800 ppm) and oxygen (5.1%). Under both conditions, n_e decreases by increasing discharge current. This reflects the increased possibility of one electron to collide with gas molecules by decreasing discharge current. When n_e is more than 1.0, one electron is supposed to remove more than one molecule of SO_2. In this calculation, we can see that one electron removes several molecules of SO_2 in the presence of oxygen. The maximum n_e in Table 4 that is 5.4 in the presence of oxygen and water vapor at 0.25 mA shows that one electron removes more than five SO_2 molecules. We recognized such high removal efficiencies in the removals of the other sulfur compounds, too.

To explain the increase of the removal efficiency by coexisting oxygen, we consider the formation of ion-clusters with sulfur compound molecules observed by Lakdawala and Moruzzi (1981). They have reported the experimental observations of clusters induced by negative ions of oxygen with several SO_2 molecules. These cluster formations can be described by Eqs. 6 and 7.

Table 4. Mean Number of SO_2 Molecules Removed by One Electron, n_e

Discharge Current $SV = 37.7\ \mathrm{h^{-1}}$ $C_{in} = 120$ ppm	In Presence of H_2O $C_{H_2O} = 3{,}700$ ppm		In Presence of H_2O and O_2 $C_{H_2O} = 3{,}800$ ppm, $C_{O_2} = 5.1\%$	
	n_e	ψ	n_e	ψ
0.25 mA	1.18	0.18	5.40	0.80
0.50 mA	0.70	0.21	3.16	0.93

$$O_2^- + n\,SO_2 \rightarrow O_2^-(SO_2)_n \quad (n = 1, 2, \ldots) \tag{6}$$

$$O^- + n\,SO_2 \rightarrow O^-(SO_2)_n \quad (n = 1, 2, \ldots) \tag{7}$$

If such clusters deposit at the anode surface, one electron should contribute to remove several molecules of sulfur compounds. We assume that the increase of removal efficiency by mixing water vapor can also be attributed to cluster formation, such as $[(OH^-)(SO_2)_n]$.

Other possibilities of reaction mechanisms are:

(1) O_3 is produced in the corona discharge reactor up to order of 3,000 ppm. To check the reactivity of O_3 with sulfur compounds, we have supplied O_3 to the reactor with CH_3SH and CS_2. By this experiment, we confirmed that the reaction of O_3 is not significant;

(2) It is reported that O reacts with CS_2 and COS to produce SO (Clough et al., 1978). This reaction might produce reaction byproducts;

(3) It is reported that it is highly possible that H^- and OH are produced when electron collides with H_2O molecule (Moruzzi et al., 1966; Massey, 1976). OH might react with sulfur compounds to produce reaction byproducts.

Despite the three possibilities listed above, it is not reasonable to think that these reactions are the main reason for high removal efficiencies of sulfur compounds. If the improved removal efficiency of sulfur compounds is attributed mainly to the above reactions, the outlet gas must contain as many reaction byproducts as reacted sulfur compounds. In fact, the outlet gas contains only traces of reaction byproducts. It suggests that the most removed sulfur compounds must deposit on the anode surface. To explain the deposit of molecules of sulfur compounds, which are more than the number of electrons to the anode, it is reasonable to think of the formation of negative-ion cluster with several molecules of sulfur compounds.

Conclusions

The removal of six sulfur compounds from nitrogen by electron attachment in the presence of oxygen and/or water vapor was conducted. As a result, we discovered that the mixture of oxygen or water vapor could increase the removal efficiency. The experimental results suggested that the present gas purification principle was applicable for removing the sulfur compounds from air. It was found that one electron contributed to remove more than five molecules of sulfur compounds in the corona-discharge reactor.

In the removal experiments, we observed reaction byproducts SO_2 and COS, which had a negative effect on the removal efficiency. In the presence of oxygen, formation of those byproducts could be decreased by using high discharge current. However, excess concentration of oxygen causes the increase of COS formation. In the removals from nitrogen-water vapor mixtures, formation of SO_2 was increased with the discharge current, which caused the decrease of the removal efficiency in the high discharge current range.

To explain the results, it was considered that the improvement of removal efficiency by mixture of these coexisting gases can be attributed to formation of negative ion-induced cluster with several molecules of sulfur compounds.

Acknowledgment

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Notation

C = concentration, ppm
E = electric field, $V \cdot m^{-1}$
I = discharge current, mA
N_{e0} = number of electrons appeared in corona discharge in unit time, s^{-1}
N_r = number of removed gas molecules in unit time, s^{-1}
p = pressure, Pa
SV = space velocity, h^{-1}

Subscripts

in = inlet of reactor
max = maximum value
out = outlet of reactor
sub = byproduct

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