SO₂ Gas Physicochemical Removal through Pulse Streamer Discharge Technique Assisted by Vapor Additive

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1. Introduction

Sulfur dioxide (SO₂) has played important roles in acid rain formation [1]. There has been natural source of this environment-polluting compound, such as the exhaust gas emitted from volcanoes [2]. But most of the SO₂ ingredients produced nowdays should be ascribed to the fuel and coal combustion [3]. The exhaust gas emission from automobiles or power plants has become deteriorating social problems for generating acid rain. The acid rain can pollute the earth soil, the water, the building surface, and the metal coatings and has drawn extensive attentions from the viewpoint of government, law legislation, and the power plants, as well as the internal-combustion engine designers [4, 5]. Severe regulations on SO₂ emissions have propelled the advancements of SO₂ removal techniques, including spray-dry or wet scrubbing and catalyst [6, 7]. Jin et al. reported that chlorine dioxide (ClO₂) gas could be utilized to clean up SO₂, and about 100% removal efficiency was achieved under optimal conditions of passing sufficient ClO₂ gas into the scrubbing solution [8]. Wang et al. found that the ozone injection plus a glass made alkaline washing tower could efficiently achieve desulfurization [9]. Rayon-based activated carbon fibers (ACFs) at temperatures of 313–348 K had exhibited high SO₂ removal activity [10]. Mn-based activated carbon catalysts were prepared, with MnO and Mn₃O₄ coexisting in catalysts, and had exhibited SO₂ removal ability [11]. Pt/CeO₂ catalysts prepared on Cu (III) had been applied to assist the transformation of SO₂ into atomic sulfur on its surface at the temperature above 300 K [12]. The Mo and Co doped V₂O₅/AC catalyst-sorbents were also used as catalyst for SO₂ removal [13].

The wet scrubbing method is effective and has the utilizing prospect for flue gas desulfurization. But it should be noticed that the wet scrubbing process should be operated in relatively large reactors and some complex chemical reactions
should be precisely controlled to generate gas-phase oxidant such as ClO$_2$ and O$_3$, exemplified by the chlorate-chloride process as

\[
2\text{H}_2\text{SO}_4 + 2\text{NaClO}_3 + 2\text{NaCl} \\
\rightarrow 2\text{ClO}_2 \uparrow + \text{Cl}_2 + 2\text{H}_2\text{O} + 2\text{Na}_2\text{SO}_4
\] (1)

The ClO$_2$ scrubber gas is usually generated on-site since ClO$_2$ can rapidly decompose through photo dissociation [14]. Despite possessing high efficiency, such wet scrubbing method has relatively high cost and should carefully dispose the end liquid waste. In addition, the design of wet scrubbing technology is highly dependent on the characteristics of the treated flue gas. Furthermore, the catalyst removing SO$_2$ reaction is operated usually under relatively high temperature.

As alternative method, the high energy e-beam (EB, electron beams) technology has also been utilized in power plants based on the mechanism of high energy electron collision on the O$_2$, H$_2$O, and so on, to generate the radical agents such as O, OH, and HO$_2$, for gas-phase oxidizing SO$_2$ in the exhaust gas [15]. There have been no or fewer amounts of wet end products, benign gas emission or easily captured aerosol dusts. The 70–98% removal efficiency had been reported through such EB method, though its disadvantage is the requirement of large space and high energy consumption, for which the injected electrons should be accelerated to several MeV magnitudes (the input power of the electron accelerator usually in the range of $10^2$ – $10^3$ kV, and the accelerator is large in space). The X-ray exposure due to the emissions sourced from the deep excited radicals and molecules is another environmental risk. Based on its inherent characters, the EB technique had been successfully applied in the thermal power plants in many countries [16].

Compared to the wet scrubbing, catalyzing, or e-beam technique, the pulsed corona discharges, pulsed streamer discharges, or dielectric barrier discharges (DBD) demonstrate the advantage of low cost, for which these pulsed discharges are generated under lower voltages ($\sim 10^4$ kV) through simpler power supply, and the discharge instruments could be miniaturized. Such pulsed discharge removing SO$_2$, NO$_x$, or other volatile organic compounds (VOC) has attracted the interests from the academic to industrial community, and successful application has been obtained in China and other countries [17, 18].

As important candidate for high-efficient SO$_2$ remediation, the pulse discharging technique can inject high energy electrons to physically dissociate the SO$_2$ molecules and further chemically transform the SO$_2$ molecules into benign or easily captured species [19, 20]. Gas additive mixed with SO$_2$ can sometimes present improvement effect. Ma et al. reported that SO$_2$ removal was improved by adding NH$_3$ into the air stream through the DBD discharge nonthermal plasma technique [21]. But the (NH$_4$)$_2$SO$_3$ or NH$_4$HSO$_3$ production after discharge is not thermally stable enough and can further decompose into SO$_2$. Since NH$_3$ additive for discharging removal of SO$_2$ is unstable, the NH$_3$ injection is usually utilized into the terminal of the pulse discharging instrument to collect the H$_2$SO$_4$ aerogel dust, and the cost of injected NH$_3$ is also expensive [22–24]. The catalyst combined plasma technique is also noticed. For example, TiO$_2$-coated glass beads had been applied for SO$_2$ removal. The SO$_2$ removal efficiency was improved by the radicals generated from plasma reactions and TiO$_2$ photo-catalyst [25].

Usually, hydroxyl (OH) radicals are highly active and can be derived from the H$_2$O decomposition [26]. The hydroxyl radical is often referred to as the “detergent” because it can react with many pollutants [27–29]. In this paper, the SO$_2$ removal physical chemistry kinetics without and with vapor additive are analyzed, and the OH improvement effect on SO$_2$ remediation is focused on. The pulse streamer discharge technique for SO$_2$ removal is introduced in Section 2. The emission spectra are detected and diagnosed for analyzing the SO$_2$ removal mechanism, and a zero-dimensional physicochemical reaction model is established in Section 3. Numerical simulation is quantitatively achieved. Section 4 announces the conclusions.

2. Experimental Section

The SO$_2$ removal system is diagramed in Figure I. The SO$_2$ is experimentally generated through the reaction between H$_2$SO$_4$ and Na$_2$SO$_3$. N$_2$ acts as carrier gas to deliver SO$_2$ gas to the discharge zone. After discharge, the residual SO$_2$ and other gaseous productions are neutralized by NaOH solution.

![Diagram of the pulse streamer discharge system for SO$_2$ removal.](image)
The pulse streamer discharge reactor is consisting of two electrodes, which are oppositely placed and encapsulated in a glass tube. High energy electrons are injected from one electrode driven by the pulse electric field and then streamed to the other electrode. During the electron streaming process, the SO2 molecules can be physically collided.

The discharge voltage is 9.5 kV, with the pulse duration of 0.5 μs. The discharge frequency is 50 Hz, which is the power frequency of China. Gas pressure in the tube is controlled at 1 atm.

In order to monitor the SO2 removal process by untouched technique, the emission spectra are collected through a quartz window on the surface of the discharge tube by monochromator (ACR, AM-566). The collected photons are transformed into electrical signal by multiplier phototube (PMT, HAMAMATSU, and CR184) and denoised and amplified by Boxcar (SRS, SRS 280/255).

3. Results and Discussion

The emission spectra are collected and diagnosed to evaluate the species categories that appeared during discharge. In order to clarify the physical chemistry reaction kinetics, a zero-dimensional physicochemical reaction model is established and numerically simulated.

3.1. Emission Spectra Diagnosis. For the pulse discharging plasma, the emission spectrum is sourced from the mechanism that the SO2 gas molecules are excited through inelastic collision by the high energy electron. Since the kinetic energy of the electrons is ruled by statistical distribution principle, the SO2 molecules are excited to energy states in a wide range. Furthermore, the more important effect of such collision is that the SO2 would be decomposed into radicals. Such radicals also can be excited [30]. Then, the irradiation emitted from the wide-range energy upstates of the excited molecules and radicals can be observed and collected. The emission spectra are presented in Figure 2. There have been complicated emission bands at the wavelength range from 200 to 500 nm.

The emission bands are evaluated. There appears the emission sequence at 337.13, 358.36, 376.94, 423.84, 440.48, and 469.24 nm, which is discriminated as N2 transition from its C1Πu excited state to B1Πg ground state [31]. The N2 appeared at the discharge zone as carrier gas as shown in Figure 1.

For the slow-varying peaks around 333.89, 373.55, and 440.12 nm, which are superposed onto the N2 emission sequence, they are evaluated as the continuous emission band of SO2 molecule and are related to the SO2 transition paths of (B1Πg → X1Σg)(A1Σg → X1Σg), and (a′B1 → X1A1), respectively [32–34]. It means that the SO2 has been excited to the B1Πg excited state through the inelastic collision by the high energy electrons. Then, the excited SO2 relaxes to its X1A1 ground state through radiation transition. For the A1A2 or a′B1 excited state of SO2, it is transferred from B1Πg state through nonradiative transition process and then relaxed to the X1A1 state by radiative transition. The electron collision onto SO2 molecule has induced complex excitation and energy transition processes.

There also has been an unattached emission peak around 237.17 nm in Figure 2, which is evaluated as the characteristic emission of sulfur monoxide (SO) from its excited A1Π state to the X1Σ state [35, 36]. SO possesses poor stability and can only be generated by dissociation of SO2 during the electron collision process. It indicates that some part of the SO2 molecules has been successfully removed through the pulse streamer discharge technique.

The possible SO2 removal routines are deduced based on the emission spectra and the evaluated transition paths as

\[ e^+ + SO_2 (X^1A_1) \rightarrow SO \left( A^1Π \right) + O \left( ^3P \right) + e \quad (2) \]

\[ SO \left( A^1Π \right) \rightarrow SO \left( X^1Σ \right) + h\nu \quad (3) \]

In (2), the SO2 in ground state of $X^1A_1$ state can be physically collided and excited by the electrons injected from the electrode in Figure 1 and dissociated into SO in $A^1Π$ excited state and O in $^3P$ ground state. Such dissociative threshold energy is about 10.36 eV [37]. The excited SO compounds further transfer to the ground state of $X^1Σ$ through radiation.

There also have been other possible routines such as

\[ e^+ + SO_2 (X^1A_1) \rightarrow SO \left( X^1Σ \right) + O \left( ^3P \right) + e \quad (4) \]

\[ e^+ + SO_2 (X^1A_1) \rightarrow SO_2 \left( A^1A_2/B^1B_1 \right) + e \quad (5) \]

\[ SO_2 \left( A^1A_2/B^1B_1 \right) \rightarrow SO \left( A^1Π/X^1Σ \right) + O \left( ^3P \right) \quad (6) \]

\[ SO \left( A^1Π \right) \rightarrow SO \left( X^1Σ \right) + h\nu \quad (7) \]

3.2. Establishment of SO2 Physicochemical Removal Dynamic Model. Due to many complex physical chemistry reactions involved, it is difficult to quantitatively analyze the SO2 removal process by experimental method. In this section,
the removal process is investigated through establishing a zero-dimensional reaction model. In order to improve the removal efficiency, the H$_2$O vapor additive is considered.

There have been two procedures for SO$_2$ removal.

3.2.1. Physical Decomposition of SO$_2$ and H$_2$O through Inelastic Collision by the Electrons. The electron collision dissociative cross sections are presented in Figure 3. It should be noticed that the dissociative energy of H$_2$O is smaller than that of SO$_2$, and cross sections of the former are higher at about 10$^3$ cm$^{-1}$ magnitude order than that of SO$_2$. H$_2$O molecule is easier to be decomposed.

For the electron collision onto SO$_2$ or H$_2$O, the physical reaction kinetics are ruled by the reaction rate coefficient, denoted as the symbol of $k$. Such rate coefficients can be calculated by solving the Boltzmann Equation of electron collision dissociative cross sections [38]. According to the cross sections in Figure 3, the rate coefficients are calculated in this paper as

$$e^+ + SO_2 \rightarrow SO + O + e \quad k = 1.16 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad (8)$$

$$e^+ + H_2O \rightarrow OH + H + e \quad k = 8.87 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}. \quad (9)$$

In pulse streamer discharging plasma, the SO$_2$ or H$_2$O molecules can be physically decomposed. The new byproduct “fragments” are SO, O, OH, H, and so forth.

3.2.2. Further Chemical Reactions between the Byproducts and SO$_2$. The produced SO, O, OH, and H are active radicals and can further chemically react with SO$_2$ or H$_2$O. There also have been other reactions. The main reaction paths are analyzed and outlined in Table 1.

After being dissociated by electron collision, the produced O radical can chemically participate in reaction for SO$_2$ removal by forming SO$_3$, or forming SO and O$_2$. The OH radicals have played important roles in the removal process, and new molecules, such as HSO$_3$, HOSO$_2$, and H$_2$SO$_4$, are synthesized. There also have been reverse reactions to transform the new products into SO$_2$ pollutant molecules. The main reaction routines are graph-outlined in Figure 4.

Based on the reaction graph, the reaction kinetics are numerically modeled as time-varying differential equation set. Every differential equation in the set is proposed based on the Arrhenius principle that the concentration of a given $i$th species (one species selected from the reacting ingredients in the model, such as SO$_2$, SO, SO$_3$, O, O$_2$, H$_2$O, OH, HO$_2$, H, HSO$_3$, HOSO$_2$, and H$_2$SO$_4$ in Table 1 and Figure 4) is changing according to the law of conservation of matter [48]. Among the reactions, there has been losing process of $i$th species caused by the reaction between $i$th and $j$th species; then, the decreased concentration in unit time, or the losing rate of concentration $dn_i/dt|_{\text{losing}}$, is described as $-k_{ij}n_in_j$, in which the symbols of $n_i$, $n_j$ denoted the respective concentration of $i$th or $j$th species and $k_{ij}$ as the rate coefficient of the reaction between $i$th and $j$th species.

All the concentration decreasing processes of $i$th species in unit time should be abstracted from the $N$ reactions about $i$th species losing processes and linear superimposed together as

$$\frac{dn_i}{dt}|_{\text{losing}} = - \sum_{j=1}^{N} k_{ij}n_in_j. \quad (10)$$

Similarly, the concentration generating processes of $i$th species in unit time, which are abstracted from all the $M$ reactions related to the $i$th species generating processes based on the reaction between species $p$th and $q$th, are denoted as

$$\frac{dn_i}{dt}|_{\text{generating}} = + \sum_{p=1}^{M} k_{pq}n_pn_q. \quad (11)$$

Table 1: Main reactions and the corresponding rate coefficients.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$k$/cm$^3$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$ + O $\rightarrow$ SO$_3$</td>
<td>$3.52 \times 10^{-14}$ [39]</td>
</tr>
<tr>
<td>SO$_2$ + O $\rightarrow$ SO + O$_2$</td>
<td>$1.17 \times 10^{-12}$ [40]</td>
</tr>
<tr>
<td>SO + O $\rightarrow$ SO$_2$</td>
<td>$5.10 \times 10^{-23}$ [40]</td>
</tr>
<tr>
<td>SO + O$_2$ $\rightarrow$ SO$_3$ + O</td>
<td>$7.60 \times 10^{-17}$ [41]</td>
</tr>
<tr>
<td>SO + SO $\rightarrow$ SO$_3$ + SO$_2$</td>
<td>$1.99 \times 10^{-15}$ [42]</td>
</tr>
<tr>
<td>SO$_2$ + OH $\rightarrow$ HSO$_3$</td>
<td>$7.40 \times 10^{-12}$ [17]</td>
</tr>
<tr>
<td>SO$_2$ + OH $\rightarrow$ HOSO$_2$</td>
<td>$1.31 \times 10^{-12}$ [41]</td>
</tr>
<tr>
<td>HSO$_3$ + OH $\rightarrow$ H$_2$SO$_4$</td>
<td>$9.80 \times 10^{-12}$ [17]</td>
</tr>
<tr>
<td>SO + OH $\rightarrow$ SO$_2$ + H</td>
<td>$8.60 \times 10^{-11}$ [43]</td>
</tr>
<tr>
<td>SO$_2$ + H $\rightarrow$ OH + SO</td>
<td>$3.06 \times 10^{-12}$ [44]</td>
</tr>
<tr>
<td>SO$_2$ + H$_2$O $\rightarrow$ H$_2$SO$_4$</td>
<td>$1.20 \times 10^{-15}$ [45]</td>
</tr>
<tr>
<td>HOSO$_2$ + O$_2$ $\rightarrow$ HO$_2$ + SO$_3$</td>
<td>$4.30 \times 10^{-13}$ [41]</td>
</tr>
<tr>
<td>SO$_2$ + HO$_2$ $\rightarrow$ OH + SO$_3$</td>
<td>$2.01 \times 10^{-17}$ [46]</td>
</tr>
<tr>
<td>H$_2$O + H $\rightarrow$ OH + H$_2$</td>
<td>$4.20 \times 10^{-12}$ [47]</td>
</tr>
<tr>
<td>OH + O $\rightarrow$ O$_2$ + H</td>
<td>$3.00 \times 10^{-11}$ [17]</td>
</tr>
</tbody>
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Further scrubbed

Then, the concentration varying process of \( i \)th species in unit time is decided by the losing and generating process and denoted as

\[
\frac{dn_i}{dt} = \frac{dn_i}{dt}_{\text{losing}} + \frac{dn_i}{dt}_{\text{generating}}
\]

\[
= -\sum_{j=1}^{N} k_{ij} n_j + \sum_{p=1}^{M} \sum_{q=1}^{M} k_{pq} n_p n_q
\]  \hspace{1cm} (12)

Through the same procedures, every kind of species in the model is corresponding to a given differential equation. Consequently, an equation set including 13 equations is established in this paper to describe the varying concentration of 13 kinds of different species. The time-resolved concentration evolutions of all species are obtained by solving this differential equation set by Runge-Kutta algorithm [49].

It should be noticed that there are no spatial variables in (12). This means that the concentrations of all the species are uniformly hypothesized. The diffusion of electrons, \( \text{SO}_2 \) molecules, and the byproducts has been ignored. Since there only has been concentration evolution of every species in time scale, a zero-dimensional physicochemical reaction model is established in this paper. During the simulation based on Table 1 and Figure 4, the discharge energy is set as 120 Td. The plasma temperature is 5000 K. The gas pressure is 1 atm, and the gaseous reactions are carried out at room temperature.

3.3. \( \text{SO}_2 \) Removal Kinetic Simulation

3.3.1. \( \text{SO}_2 \) Removal Physicochemical Kinetics without \( \text{H}_2\text{O} \) Vapor Additive. According to the reaction model without vapor additive, \( \text{SO}_2 \) can be dissociated by electron collision during discharge. To clarify the removal kinetics, time-resolved concentration evolution of \( \text{SO}_2 \), \( \text{O} \), and \( \text{SO} \) and further oxidized species such as \( \text{O}_2 \) and \( \text{SO}_3 \) are presented in Figure 5.

In Figure 5(a), the \( \text{SO}_2 \) concentration is varied at a monotonic decreasing trend when discharge time increased. The \( \text{SO}_2 \) removal has obviously been achieved through the pulse streamer discharge technique. After discharge lasted for 0.5 \( \mu s \), the removal efficiency is about 0.296\%, which is leanly low. Most of the removed \( \text{SO}_2 \) has been transformed to \( \text{SO} \) and \( \text{O}_2 \) as shown in Figure 5(b), with the former concentration accumulating to \( 7.163 \times 10^{16} \text{ cm}^{-3} \) and the latter to \( 3.458 \times 10^{16} \text{ cm}^{-3} \). For the \( \text{SO}_3 \), its final concentration is about \( 1.082 \times 10^{15} \text{ cm}^{-3} \). When it comes to the \( \text{O} \) radicals, there appears an accumulating trend during discharge and concentration of \( 2.506 \times 10^{15} \text{ cm}^{-3} \) has been accumulated. After discharge, the \( \text{O} \) species have been fast consumed out to be zero to form \( \text{SO}_3 \), \( \text{SO}_2 \), and \( \text{O}_2 \).

The removal process of the \( \text{SO}_2 \) is deduced as two procedures. The first is the decomposition of \( \text{SO}_2 \) into \( \text{SO} \) and \( \text{O} \). The second is the oxidation process, during which the \( \text{O}_2 \) is easier to be generated through the reaction between \( \text{O} \) and \( \text{SO}_2 \) with a higher reaction rate coefficient of \( 1.17 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) than that for forming \( \text{SO}_3 \) of \( 3.52 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \). The \( \text{O} \) radical decomposed from \( \text{SO}_2 \) during discharge has played the key roles in the \( \text{SO}_2 \) removal process under the hypothesis without \( \text{H}_2\text{O} \) vapor additive.

The injected electrical energy is essential to influence the \( \text{SO}_2 \) removal efficiency. With the discharge pulse duration widened, the inputted electron concentration is increased. Under such a variance, the removal efficiency of \( \text{SO}_2 \) is presented in Figure 6. There appears an increasing trend of the removal efficiency with the pulse duration heightened. In the same reaction model, more electrons injection induces more \( \text{SO}_2 \) to be physically decomposed. The further chemical reactions for forming \( \text{O}_2 \), \( \text{SO}_3 \), and so on are then accelerated.

Under the discharge pulse with duration of 3 \( \mu s \), which bears six times energy compared to the pulse with duration of 0.5 \( \mu s \), the removal efficiency has only heightened to 1.796\%. From the viewpoint of energy consumption, such \( \text{SO}_2 \) removal through direct decomposition by electron inelastic collision has high cost and low efficiency.

3.3.2. Vapor Additive Effect on \( \text{SO}_2 \) Physicochemical Removal Kinetics. Without \( \text{H}_2\text{O} \) vapor added, the \( \text{SO}_2 \) removal efficiency is very low. To improve the removal process, the \( \text{H}_2\text{O} \) vapor is considered, which is usually mixed in the \( \text{SO}_2 \) exhaust gases and the out-injecting \( \text{H}_2\text{O} \) vapor is also very easy and cheap. According to the reaction model in Table 1 and Figure 4, the \( \text{OH} \) and \( \text{H} \) radicals, decomposed from
H₂O molecules by electron collision, can participate in many chemical reactions related to SO₂ or the radicals. Even the H₂O itself can transform SO₃ into H₂SO₄. More effective removal is expected. But the attenuation effect of the OH radical should be noticed, by which the SO can be reversely transformed into SO₂.

In Figure 7, the time-resolved concentration variance of SO₂ and all other byproducts is presented under the initial concentration ratio between H₂O and SO₂ of 0.1:1. The discharge pulse duration is the same as that in Figure 5 of 0.5 μs. Compared to the 0.296% removal efficiency in Figure 5, the removal efficiency is remarkably improved by H₂O vapor additive, and higher removal efficiency of 13.0195% has been finally achieved in Figure 7(a). Such variance is ascribed to the reason that the injected electrons are effectively utilized by H₂O, and the produced H and OH radicals have efficiently accelerated the SO₂ removal kinetics, which can be verified from the byproduct concentration variance in Figures 7(b), 7(c), and 7(d).

In Figure 7(b), the SO₃ formation is affected by vapor additive. Its final concentration is about 3.90 × 10¹⁵ cm⁻³, which is at the same magnitude order as that without vapor additive. But a monotonic increasing trend for the SO₃ concentration appeared, which is due to the HO₂ oxidizing SO₂ and the reaction between HOSO₂ and O₂, though O radicals have been consumed out after discharge.

The obvious increment occurred for SO concentration in Figure 7(b), which has accumulated to 1.036 × 10¹⁸ cm⁻³ after 0.5 μs, and is higher than that without vapor additive of 7.163 × 10¹⁶ cm⁻³ at 10³ cm⁻³ magnitude order. Such a remarkable increment is decided by the H radicals, which are directly decomposed from H₂O molecules. The H radical can react with SO₂ to produce SO and OH and is formulated in (13). Vapor additive has accelerated the SO generation efficiency:

\[
SO_2 + H \rightarrow OH + SO \quad k = 3.06 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}. \tag{13}
\]

More OH production is beneficial to the O₂ generation according to

\[
OH + O \rightarrow O_2 + H \quad k = 3.00 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}. \tag{14}
\]

But the O₂ concentration of only 3.049 × 10¹⁶ cm⁻³ has been obtained after 0.5 μs in Figure 7(b), which is slightly lower than 3.458 × 10¹⁶ cm⁻³ without H₂O vapor added. The decrement is ascribed to the consumption of OH not only by O to produce O₂ as ruled by (14), but also by other reaction paths to produce HSO₃, HOSO₂, H₂SO₄, or even SO₃ as shown in Table 1. And the consumption of O₂ by HOSO₂ and SO is another important reason for the decrement of O₂ concentration.

The concentrations of HSO₃ and HOSO₂ in Figure 7(c) have accumulated to 1.736 × 10¹⁸ and 0.724 × 10¹⁸ cm⁻³, respectively. For the former, it has become the major production due to its highest final concentration. There also has been 0.093 × 10¹⁸ cm⁻³ H₂SO₄ produced through the reaction between SO₃ and H₂O or between HSO₃ and OH.

**Figure 5:** Without H₂O vapor added, (a) time-resolved evolution of SO₂ concentration and the removal efficiency, and (b) time-resolved concentration evolution of SO, O₂, O, and SO₃.

**Figure 6:** Relationship between SO₂ removal efficiency and the discharge pulse duration.
And the concentration of HO₂ is about 0.084 × 10^{18} \text{cm}^{-3} in Figure 7(c). Such low concentrations imply that both H₂SO₄ and HO₂ are not the main final productions under the initial H₂O/SO₂ ratio of 0.1:1.

All such concentration variances are decided by the H₂O physical decomposition into H and OH through electron inelastic collision, and the H₂O has been consumed with its final concentration decrement amount of about 1.2802 × 10^{18} \text{cm}^{-3} after discharge lasted for 0.5 \mu s in Figure 7(d). And the OH radicals have played the major roles for SO₂ removal to transfer SO₂ into HSO₃:

\[ \text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3 \quad k = 7.40 \times 10^{-12} \text{cm}^3\text{s}^{-1}. \quad (15) \]

When the concentration ratio between H₂O and SO₂ is 0.1:1, the major productions are HSO₃ with a little HOSO₄, and the H₂SO₄ concentration is lower than them with 10² cm⁻³ magnitude orders. For SO₂ removal, the main production is expected to be H₂SO₄, since H₂SO₄ is chemically stable and can be easily neutralized by alkali or captured by fabric filter or electrostatic precipitator (ESP). In order to adjust the final productions, the vapor ratio is varied in Figure 8. It presents that the higher the vapor ratio is, the more the H₂SO₄ molecules have been produced. The H₂SO₄ concentration is even higher than that of HSO₃ when the initial vapor/SO₂ concentration ratio is above 1.27:1.

H₂O additive with higher ratio has generated more OH radicals and consequently accelerated the reactions between HSO₃ and OH as

\[ \text{HSO}_3 + \text{OH} \rightarrow \text{H}_2\text{SO}_4 \quad k = 9.80 \times 10^{-12} \text{cm}^3\text{s}^{-1}. \quad (16) \]

by which the HSO₃ has been transformed into H₂SO₄. Such reaction has simultaneously decreased the HSO₃ concentration and increased the H₂SO₄ concentration, as shown in Figure 8(a). More vapor additive has effectively adjusted the SO₂ removal physicochemical kinetics to the favorite directions, and H₂SO₄ has become the major production when the initial vapor mixing ratio is above 1.27:1.

For other species such as HOSO₂ and SO in Figure 8(a), the former is increased at a monotonic trend, but its highest final concentration at vapor ratio of 2:1 is obviously lower than that of H₂SO₄. The latter SO is increased at low vapor ratio and decreased at high vapor ratio. Such varying trends of
HOSO$_2$ and SO are ascribed to the more OH decomposed at higher vapor ratio. The HOSO$_2$ concentration is heightened through the reaction between OH and SO$_2$, and the SO concentration is decreased by the reaction between OH and SO to reproduce SO$_2$. Such reactions are formulated as follows:

$$\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2 \quad k = 1.31 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$$ (17)

$$\text{SO} + \text{OH} \rightarrow \text{SO}_2 + \text{H} \quad k = 8.60 \times 10^{-11} \text{ cm}^3\text{s}^{-1}.$$ (18)

In conclusion, vapor additive has effectively improved the SO$_2$ removal efficiency in Figure 8(b). In the simulation, even 89.1% removal efficiency has been achieved at the initial concentration ratio of 2:1 between H$_2$O and SO$_2$.

### 4. Conclusions

SO$_2$ removal is important for air pollution treatment. In this paper, the pulse streamer discharge technique is investigated. Emission spectra diagnosis implies that the SO$_3$ molecules have been physically dissociated by the injected electrons and transformed into SO and O. In order to quantitatively clarify the complex removal kinetics, a zero-dimensional physicochemical simulating model is established. Simulation indicates that the SO$_2$ removal without H$_2$O vapor additive is leanly achieved with the final efficiency of only 0.296%. The injected electrical energy can improve the removal efficiency, and an increment trend is presented with the pulse duration increased. But the improvement is not very notable. After six times concentration of electrons injected, the SO$_2$ removal efficiency is increased from 0.296% at the pulse duration of 0.5 $\mu$s to only 1.80% at the pulse duration of 3 $\mu$s. In order to improve the removal process, the H$_2$O vapor additive is applied. Under the pulse duration of 0.5 $\mu$s and the initial concentration ratio between H$_2$O and SO$_2$ at 0.1:1, there appears remarkable increment of the SO$_2$ removal efficiency as 13.0195%. But the major productions are HSO$_3$ and HOSO$_2$, and H$_2$SO$_4$ concentration is lower than them with $10^3$ cm$^{-3}$ magnitude order. More H$_2$O additive has generated more OH radicals, which effectively adjusted the SO$_2$ physicochemical removal process to the favorite directions. H$_2$SO$_4$ has become major production when initial vapor ratio is above 1.27:1. Even 89.1% removal efficiency has been achieved at the concentration ratio of 2:1 between H$_2$O and SO$_2$.

From the viewpoint of energy consumption and pollutant gas removal efficiency, the H$_2$O vapor additive is verified and effective enough to be considered for commercial applications in pulse streamer discharge system for SO$_2$ removal.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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