

Research Article

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

Xiaojun Wang¹ and Lianshui Zhang²

¹Science and Technology College, North China Electric Power University, Baoding, Hebei 071051, China
²College of Physics Science and Technology, Hebei University, Baoding, Hebei 071000, China

Correspondence should be addressed to Lianshui Zhang; zhanglshbu@sina.com

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 SO_2 removal has drawn extensive attentions for air pollution treatment. In this paper, the pulse streamer discharge technique is investigated. Emission spectra diagnosis experimentally indicates that the SO_2 molecule has been physically dissociated into SO and O radicals by electron collision and can be remediated through further chemical reactions during and after discharge. In order to quantitatively analyze the removal physical chemistry kinetics, a zero-dimensional physicochemical reaction model is established. Without H₂O vapor additive, the SO₂ removal efficiency is leanly low and only 0.296% has been achieved under pulse discharge duration of 0.5 μ s. Through increasing the electrical concentration six times, the removal efficiency has been slightly heightened to 1.796% at pulse duration of 3 μ s. Contrarily, vapor additive can effectively improve the removal kinetics, and removal efficiency has been remarkably heightened to 13.0195% at pulse duration of 0.5 μ s with H₂O/SO₂ initial concentration ratio of 0.1:1. OH radicals decomposed from H₂O through electron collision are the essential factor to achieve such improvement, which have effectively adjusted the chemical removal process to the favorite directions. The major productions have been transformed from HSO₃ and HOSO₂ to H₂SO₄ when vapor ratio increased above 1.27:1.

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 nowadays 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

 SO_2 , and about 100% removal efficiency was achieved under optimal conditions of passing sufficient ClO_2 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 SO_2 removal activity [10]. Mn-based activated carbon catalysts were prepared, with MnO and Mn_3O_4 coexisting in catalysts, and had exhibited SO_2 removal ability [11]. Pt/CeO₂ catalysts prepared on Cu (111) had been applied to assist the transformation of SO_2 into atomic sulfur on its surface at the temperature above 300 K [12]. The Mo and Co doped V_2O_5/AC catalyst-sorbents were also used as catalyst for SO_2 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



FIGURE 1: Diagram of the pulse streamer discharge system for SO₂ removal.

should be precisely controlled to generate gas-phase oxidant such as ClO_2 and O_3 , exampled by the chlorate-chloride process as

$$2H_2SO_4 + 2NaClO_3 + 2NaCl$$

$$\longrightarrow 2ClO_2 \uparrow + Cl_2 + 2H_2O + 2Na_2SO_4$$
(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 SO₂ 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 O₂, H₂O, and so on, to generate the radical agents such as O, OH, and HO₂, for gas-phase oxidizing SO₂ in the exhaust gas [15]. There have been no or fewer amounts of wet end products, benign gas emission or easily captured aerogel 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 $10^2 \sim 10^3$ 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 ($\sim 10^1$ kV) through simpler power supply, and the discharge instruments could be miniaturized. Such pulsed discharge removing SO₂, 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 SO₂ remediation, the pulse discharging technique can inject high energy electrons to physically dissociate the SO₂ molecules and further chemically transform the SO₂ molecules into benign or easily captured species [19, 20]. Gas additive mixed with SO₂ can sometimes present improvement effect. Ma et al. reported that SO₂ removal was improved by adding NH₃ into the air stream through the DBD discharge nonthermal plasma technique [21]. But the $(NH_4)_2SO_3$ or NH_4HSO_3 production after discharge is not thermally stable enough and can further decompose into SO₂. Since NH₃ additive for discharging removal of SO₂ is unstable, the NH₃ injection is usually utilized into the terminal of the pulse discharging instrument to collect the H₂SO₄ aerogel dust, and the cost of injected NH₃ is also expensive [22-24]. The catalyst combined plasma technique is also noticed. For example, TiO₂-coated glass beads had been applied for SO₂ removal. The SO₂ removal efficiency was improved by the radicals generated from plasma reactions and TiO₂ photo-catalyst [25].

Usually, hydroxyl (OH) radicals are highly active and can be derived from the H_2O 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 SO₂ removal system is diagramed in Figure 1. The SO₂ is experimentally generated through the reaction between H_2SO_4 and Na_2SO_3 . N_2 acts as carrier gas to deliver SO₂ gas to the discharge zone. After discharge, the residual SO₂ and other gaseous productions are neutralized by NaOH solution.

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 μ s. 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 SO_2 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 SO_2 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 SO_2 molecules are excited to energy states in a wide range. Furthermore, the more important effect of such collision is that the SO_2 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 $C^3\Pi_u$ excited state to $B^3\Pi_g$ 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 (B¹B₁ \rightarrow X¹A₁), (A¹A₂ \rightarrow X¹A₁), and (a³B₁ \rightarrow X¹A₁), respectively [32–34]. It means that the SO₂ has been excited to the B¹B₁ 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 a³B₁ excited state of SO₂, it is transferred from B¹B₁ state through nonradiative transition process and then relaxed to the X¹A₁ state by radiative transition. The electron



FIGURE 2: The emission spectra detected from the pulse discharge SO_2 removal system in the wavelength range from 200 to 500 nm.

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 $A^3\Pi$ state to the $X^3\Sigma$ 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

$$e^* + SO_2(X^1A_1) \longrightarrow SO(A^3\Pi) + O(^3P) + e$$
 (2)

$$SO(A^{3}\Pi) \longrightarrow SO(X^{3}\Sigma) + h\nu$$
 (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 $A^3\Pi$ 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 $X^3\Sigma$ through radiation.

There also have been other possible routines such as

$$e^* + SO_2(X^1A_1) \longrightarrow SO(X^3\Sigma) + O(^3P) + e$$
 (4)

$$e^* + SO_2 \left(X^1 A_1 \right) \longrightarrow SO_2 \left(A^1 A_2 / B^1 B_1 \right) + e$$
 (5)

$$SO_2(A^1A_2/B^1B_1) \longrightarrow SO(A^3\Pi/X^3\Sigma) + O(^3P)$$
 (6)

$$SO(A^{3}\Pi) \longrightarrow SO(X^{3}\Sigma) + h\nu$$
 (7)

3.2. Establishment of SO_2 Physicochemical Removal Dynamic Model. Due to many complex physical chemistry reactions involved, it is difficult to quantitatively analyze the SO_2 removal process by experimental method. In this section,



FIGURE 3: The relationship between electron collision dissociative cross sections and the collision energy.

the removal process is investigated through establishing a zero-dimensional reaction model. In order to improve the removal efficiency, the $\rm H_2O$ vapor additive is considered.

There have been two procedures for SO₂ removal.

3.2.1. Physical Decomposition of SO₂ and H₂O 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 H₂O is smaller than that of SO₂, and cross sections of the former are higher at about 10^1 cm² magnitude order than that of SO₂. H₂O molecule is easier to be decomposed.

For the electron collision onto SO_2 or H_2O , 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

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

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

In pulse streamer discharging plasma, the SO_2 or H_2O 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_2O . 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 SO₂ removal by forming SO₃, or forming SO and O₂. The OH radicals have played important roles in the removal process, and new molecules, such as HSO₃, HOSO₂, and H₂SO₄,

TABLE 1: Main reactions and the corresponding rate coefficients.

Reactions	$k/\mathrm{cm}^3\mathrm{s}^{-1}$
$SO_2 + O \rightarrow SO_3$	3.52×10^{-14} [39]
$SO_2 + O \rightarrow SO + O_2$	1.17×10^{-12} [40]
$SO + O \rightarrow SO_2$	5.10×10^{-31} [40]
$SO + O_2 \rightarrow SO_2 + O$	7.60×10^{-17} [41]
$SO_3 + SO \rightarrow SO_2 + SO_2$	1.99×10^{-15} [42]
$SO_2 + OH \rightarrow HSO_3$	7.40×10^{-12} [17]
$SO_2 + OH \rightarrow HOSO_2$	1.31×10^{-12} [41]
$\text{HSO}_3 + \text{OH} \rightarrow \text{H}_2\text{SO}_4$	9.80×10^{-12} [17]
$SO + OH \rightarrow SO_2 + H$	8.60×10^{-11} [43]
$SO_2 + H \rightarrow OH + SO$	3.06×10^{-12} [44]
$SO_3 + H_2O \rightarrow H_2SO_4$	1.20×10^{-15} [45]
$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	4.30×10^{-13} [41]
$SO_2 + HO_2 \rightarrow OH + SO_3$	2.01×10^{-17} [46]
$H_2O + H \rightarrow OH + H_2$	4.20×10^{-12} [47]
$OH + O \rightarrow O_2 + H$	3.00×10^{-11} [17]

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 SO₂, SO, SO₃, O, O₂, H₂O, OH, HO₂, H, HSO₃, HOSO₂, and H₂SO₄ 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

$$\left. \frac{dn_i}{dt} \right|_{\text{losing}} = -\sum_{j=1}^N k_{ij} n_i n_j.$$
(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

$$\left. \frac{dn_i}{dt} \right|_{\text{generating}} = + \sum_{\substack{p=1,\\q=1}}^M k_{pq} n_p n_q.$$
(11)



FIGURE 4: Diagram of main reaction paths and species produced during discharge.

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

$$\frac{dn_i}{dt} = \left. \frac{dn_i}{dt} \right|_{\text{losing}} + \left. \frac{dn_i}{dt} \right|_{\text{generating}}$$
$$= -\sum_{j=1}^N k_{ij} n_i n_j + \sum_{\substack{p=1, \\ q=1}}^M k_{pq} n_p n_q.$$
(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, 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. SO₂ Removal Kinetic Simulation

3.3.1. SO_2 Removal Physicochemical Kinetics without H_2O Vapor Additive. According to the reaction model without vapor additive, SO_2 can be dissociated by electron collision during discharge. To clarify the removal kinetics, timeresolved concentration evolution of SO_2 , O, and SO and further oxidized species such as O_2 and SO_3 are presented in Figure 5.

In Figure 5(a), the SO_2 concentration is varied at a monotonic decreasing trend when discharge time increased. The 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 SO₂ has been transformed to SO and O₂ as shown in Figure 5(b), with the former concentration accumulating to 7.163 × 10¹⁶ cm⁻³ and the latter to 3.458 × 10¹⁶ cm⁻³. For the SO₃, its final concentration is about 1.082 × 10¹⁵ cm⁻³. When it comes to the O radicals, there appears an accumulating trend during discharge and concentration of 2.506 × 10¹⁵ cm⁻³ has been accumulated. After discharge, the O species have been fast consumed out to be zero to form SO₃, SO, and O₂.

The removal process of the SO₂ is deduced as two procedures. The first is the decomposition of SO₂ into SO and O. The second is the oxidation process, during which the O₂ is easier to be generated through the reaction between O and SO₂ with a higher reaction rate coefficient of 1.17 × 10^{-12} cm³s⁻¹ than that for forming SO₃ of 3.52×10^{-14} cm³s⁻¹. The O radical decomposed from SO₂ during discharge has played the key roles in the SO₂ removal process under the hypothesis without H₂O vapor additive.

The injected electrical energy is essential to influence the SO_2 removal efficiency. With the discharge pulse duration widened, the inputted electron concentration is increased. Under such a variance, the removal efficiency of 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 SO_2 to be physically decomposed. The further chemical reactions for forming O_2 , SO_3 , and so on are then accelerated.

Under the discharge pulse with duration of 3μ s, which bears six times energy compared to the pulse with duration of 0.5 μ s, the removal efficiency has only heightened to 1.796%. From the viewpoint of energy consumption, such SO₂ removal through direct decomposition by electron inelastic collision has high cost and low efficiency.

3.3.2. Vapor Additive Effect on SO_2 Physicochemical Removal Kinetics. Without H_2O vapor added, the SO_2 removal efficiency is very low. To improve the removal process, the H_2O vapor is considered, which is usually mixed in the SO_2 exhaust gases and the out-injecting H_2O vapor is also very easy and cheap. According to the reaction model in Table 1 and Figure 4, the OH and H radicals, decomposed from



FIGURE 5: Without H_2O vapor added, (a) time-resolved evolution of SO_2 concentration and the removal efficiency, and (b) time-resolved concentration evolution of SO, O_2 , O, and SO_3 .



FIGURE 6: Relationship between SO_2 removal efficiency and the discharge pulse duration.

 H_2O molecules by electron collision, can participate in many chemical reactions related to SO₂ or the radicals. Even the H_2O itself can transform SO₃ into H_2SO_4 . 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 SO_2 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 μ s. 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 3.90×10^{15} 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 1.036×10^{18} cm⁻³ after 0.5 μ s, and is higher than that without vapor additive of 7.163 × 10^{16} cm⁻³ at 10^2 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:

$$SO_2 + H \longrightarrow OH + SO \quad k = 3.06 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}.$$
 (13)

More OH production is beneficial to the O₂ generation according to

$$OH + O \longrightarrow O_2 + H \quad k = 3.00 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}.$$
 (14)

But the O_2 concentration of only 3.049×10^{16} cm⁻³ has been obtained after $0.5 \,\mu s$ in Figure 7(b), which is slightly lower than 3.458×10^{16} cm⁻³ without H₂O vapor added. The decrement is ascribed to the consumption of OH not only by O to produce O_2 as ruled by (14), but also by other reaction paths to produce HSO₃, HOSO₂, H₂SO₄, or even SO₂ as shown in Table 1. And the consumption of O_2 by HOSO₂ and SO is another important reason for the decrement of O_2 concentration.

The concentrations of HSO₃ and HOSO₂ in Figure 7(c) have accumulated to 1.736×10^{18} and 0.724×10^{18} cm⁻³, respectively. For the former, it has become the major production due to its highest final concentration. There also has been 0.093×10^{18} cm⁻³ H₂SO₄ produced through the reaction between SO₃ and H₂O or between HSO₃ and OH.



FIGURE 7: Under H_2O/SO_2 initial ratio of 0.1:1 and discharge pulse duration of 0.5 μ s, time-resolved evolution of (a) SO_2 concentration and the corresponding removal efficiency, (b) SO, O_2 , SO_3 , and O concentration, (c) HSO_3 , $HOSO_2$, H_2SO_4 , H, OH, and HO_2 concentration, and (d) H_2O concentration.

And the concentration of HO₂ is about $0.084 \times 10^{18} \text{ cm}^{-3}$ 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} cm⁻³ after discharge lasted for 0.5 μ s in Figure 7(d). And the OH radicals have played the major roles for SO₂ removal to transfer SO₂ into HSO₃:

$$SO_2 + OH \longrightarrow HSO_3$$
 $k = 7.40 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$. (15)

When the concentration ratio between H_2O and SO_2 is 0.1:1, the major productions are HSO_3 with a little $HOSO_2$, and the H_2SO_4 concentration is lower than them with 10^2 cm^{-3} magnitude orders. For SO_2 removal, the main production is expected to be H_2SO_4 , since H_2SO_4 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 H_2SO_4 molecules have been produced. The H_2SO_4 concentration is even higher than that of HSO_3 when the initial vapor/SO₂ concentration ratio is above 1.27 : 1.

 H_2O additive with higher ratio has generated more OH radicals and consequently accelerated the reactions between HSO_3 and OH as

$$HSO_3 + OH \longrightarrow H_2SO_4 \quad k = 9.80 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$$
 (16)

by which the HSO₃ has been transformed into H_2SO_4 . Such reaction has simultaneously decreased the HSO₃ concentration and increased the H_2SO_4 concentration, as shown in Figure 8(a). More vapor additive has effectively adjusted the SO₂ removal physicochemical kinetics to the favorite directions, and H_2SO_4 has become the major production when the initial vapor mixing ratio is above 1.27:1.

For other species such as $HOSO_2$ 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 H_2SO_4 . The latter SO is increased at low vapor ratio and decreased at high vapor ratio. Such varying trends of

 $imes 10^{19}$ 100 1.5 H_2SO_4 SO_2 removal efficiency η (%) Final concentration (cm⁻³) 80 1.2 60 0.9 HSO 0.6 40 1 27.1 0.3 20 HOSO₂ 0.0 SO 0.0 0.0 0.5 1.0 2.0 :1 1.5 2.0:1 0.5 1.0 1.5 0.0 H₂O:SO₂ ratio (a.u.) H₂O:SO₂ ratio (a.u.) (b) (a)

FIGURE 8: Under different initial vapor additive ratio, (a) the final concentration of H_2SO_4 , HSO_3 , $HOSO_2$, and SO and (b) the SO₂ removal efficiency after discharge lasted for 0.5 μ s.

 $HOSO_2$ 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:

$$SO_2 + OH \longrightarrow HOSO_2$$
 $k = 1.31 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ (17)

$$SO + OH \longrightarrow SO_2 + H$$
 $k = 8.60 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$. (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_2O and SO_2 .

4. Conclusions

SO₂ removal is important for air pollution treatment. In this paper, the pulse streamer discharge technique is investigated. Emission spectra diagnosis implies that the SO₂ 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 SO₂ removal without H₂O 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 SO₂ 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 H₂O vapor additive is applied. Under the pulse duration of $0.5 \,\mu s$ and the initial concentration ratio between H₂O and SO₂ at 0.1:1, there appears remarkable increment of the SO₂ removal efficiency as 13.0195%. But the major productions are HSO₃ and HOSO₂, and H₂SO₄ concentration is lower than them with 10^2 cm⁻³ magnitude order. More H₂O additive has generated more OH radicals, which effectively adjusted the SO₂ physicochemical removal process to the favorite directions. H₂SO₄ 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 H₂O and SO₂.

From the viewpoint of energy consumption and pollutant gas removal efficiency, the H_2O 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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