

# Kinetic model of non-thermal plasma flue gas desulfurization in a wet reactor

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## Abstract

A model of the process in a wet reactor for flue gas desulfurization by corona discharges is provided. Through deriving dependences of chain length  $\Theta$ , desulfurization rate of the flue gas upon the parameters of injected energy density  $q$ , pH values of the liquid absorbents and mass transfer efficiency factor  $\varphi$  it is found that under the conditions of given energy injection of corona discharges the flue gas desulfurization rate can be remarkably increased when the pH value is appropriately adjusted and the inner surface of the wet plasma reactor is appropriately porous. It is realizable that the energy consumption can be reduced to lower than 2–4 Wh/N m<sup>3</sup>, which is acceptable for industrial application.

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## 1. Introduction

In 1998 [1], the chemical kinetic process of non-thermal plasma flue gas desulfurization was first successfully explained on the basis of heterogeneous reactions on the interfaces between the gas and liquid film formed on the solid surfaces in a dry reactor. In that case why not adopt wet reactors to realize the process. In fact years ago many researchers tried to observe non-thermal plasma flue gas desulfurization in a wet environment. In 2000, Tseng [2] investigated the removal of SO<sub>2</sub> and NO<sub>x</sub> from combustion gas in a wet electrostatic precipitator. After that Kinoshita et al. [3] used wetted paper as the lining of a cylindrical reactor with corona wire set coaxially. The paper lining was wetted with ammonium persulfate solution to promote the oxidation of the absorbed SO<sub>2</sub>. The desulfurization rate reached 95%, the energy consumption was 22 kJ/N m<sup>3</sup>, which was higher than the experimental results in the dry reactor [1], and the byproducts are sulfates. However wet technology for non-thermal plasma flue gas desulfurization in a practical sense remains to be further developed. In addition before developing the technology with test rigs it is necessary and economic to model the process and predict the effects probably arising.

This work is devoted to model the process in a wet reactor for flue gas desulfurization by streamer discharge plasmas on the basis of widely accepted chemical kinetics so as to predict the effects probably arising in wet plasma reactors.

## 2. Description of the model

Consider a vertical round cylindrical (Fig. 1) reactor with a corona wire set coaxially. A pulsed high voltage is exerted on the wire so that streamer plasmas are emitted from it. The flue gas flows into the reactor from the top end at a given volumetric speed  $Q$  and an absorption buffer solution with a given pH is injected into the lining of the cylinder from the top. In order to simplify mathematical derivation, suppose the linear downward flow speed of the liquid is much smaller than the linear speed of the gas so that the liquid can be considered motionless relative to the gas. In addition because the gas is in the dilute phase of S(IV) in comparison to the liquid it is also reasonable to consider that the absorbed SO<sub>2</sub> does not exceed the buffer capacity so that the pH value is approximately constant. Besides, the buffer does not contain any inhibitors and catalysts which influence the reactions of our concern. These assumptions make it easy to find the characteristics related to the plasma processes to be investigated. The lining of the reactor is porous and wettable to promote the gas-to-liquid mass transfer. Define mass transfer

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### Nomenclature

$C_A$	mole concentration of solute A ( $\text{mol m}^{-3}$ )
$D$	molecular diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$G(\text{S(IV)})$	energy efficiency, the moles of the oxidized sulfite in the liquid phase per unit energy ( $\text{mol J}^{-1}$ )
$G(\text{OH})$	moles of OH radical generated by one Joule corona discharge energy ( $\text{mol J}^{-1}$ )
$H_A$	Henry's constant of gas A ( $\text{mol Pa}^{-1} \text{m}^{-3}$ )
$k_i$	rate constant of the $i$ th reaction ( $\text{m}^3 \text{s}^{-1} \text{mol}^{-1}$ )
$K$	the first ionization constant the dissolved $\text{SO}_2$ ( $\text{mol m}^{-3}$ )
$K'$	the second ionization constant the dissolved $\text{SO}_2$ ( $\text{mol m}^{-3}$ )
$l_0$	thickness of the liquid film (m)
$L$	the length of the reactor cylinder (m)
$n$	the $n$ th segment of $L$
$N$	$L$ is divided into $N$ segments
$P_A$	partial pressure of gas A (Pa)
$P_{\text{SO}_2}(0)$	the initial partial pressure of $\text{SO}_2$ (Pa)
$P_{\text{SO}_2}(L)$	the partial pressure of $\text{SO}_2$ at the exit (Pa)
$q$	streamer corona energy density ( $\text{W m}^{-3}$ )
$Q$	volumetric speed of the gas ( $\text{m}^3/\text{s}$ )
$r$	the inner radius of the reactor (m)
$\text{SO}_n^-$	the average concentration of $\text{SO}_3^-$ , $\text{SO}_4^-$ and $\text{SO}_5^-$ ( $\text{mol m}^{-3}$ )

### Greek symbols

$\gamma$	apparent chain length, generated sulfates in the experiment per consumed OH radical
$\zeta(P_{\text{SO}_2})$	the moles of the generated sulfates per unit volume per second ( $\text{mol s}^{-1} \text{m}^{-3}$ )
$\eta_{\text{SO}_2}$	$\text{SO}_2$ removal rate (%)
$\theta$	turbulent factor, for pure molecular diffusion $\theta = 1$ , when convection exists $\theta > 1$
$\Theta$	chain length generated sulfates in the theory per consumed OH radical
$\tau_{\text{OH}}$	life time of OH radical in the gas ( $= (3.0-6.0) \times 10^{-5} \text{ s}$ )
$\phi$	mass transfer efficiency factor = (the effective area of the inner surface of the reactor for receiving transferred gas) / (the area of the envelop of the inner surface)

efficiency factor  $\phi$  as the total area of the lining exposed to the corona divided by the area of the envelope of the inner surface of the lining.

In consideration of the electric wind effect, dissolution of  $\text{SO}_2$  and  $\text{O}_2$  to the liquid can be approximately equal to their Henry constants  $H_{\text{SO}_2}$  and  $H_{\text{O}_2}$  times their partial pressures  $P_{\text{SO}_2}$  and  $P_{\text{O}_2}$ , respectively, when the residence time of the gas in the reactor is sufficiently long. With salt effects taken into account,  $H_{\text{SO}_2} = 5 \times 10^{-3}$  and  $H_{\text{O}_2} = 1 \times 10^{-6} \text{ mol Pa}^{-1} \text{m}^{-3}$  [1]. In our case only the radial gas diffusion is taken into account because of the strong electric wind in the radial direction.

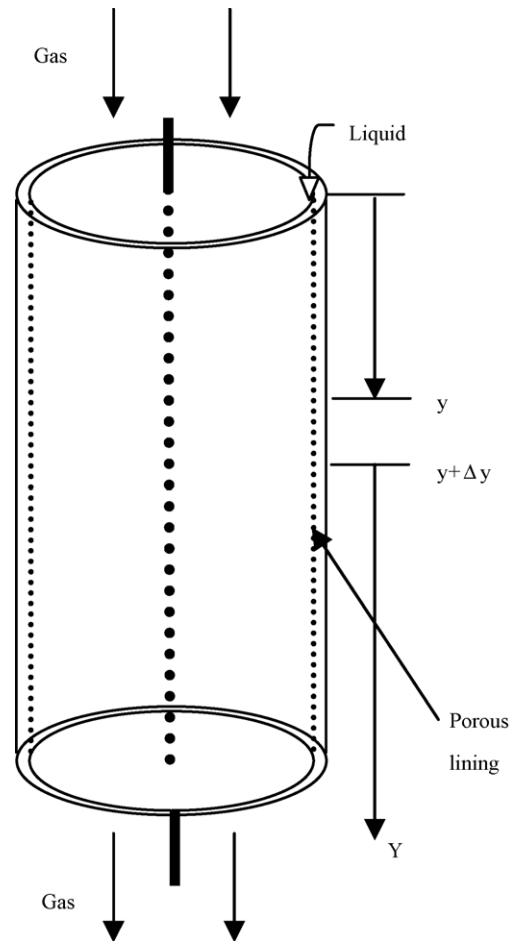
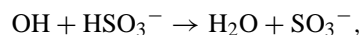
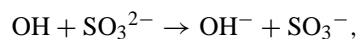


Fig. 1. A vertical round cylindrical reactor with a corona wire set coaxially and the reacting gas and liquid film within a thin sheet of the system.

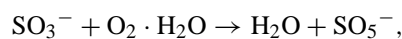
With the action of the corona discharge plasmas, the generated radicals are injected to the liquid film and initiate chain reactions to oxidize the tetravalent sulfur compounds S(IV) in the liquid phase. According to Huie, the reactions are [4,5]:



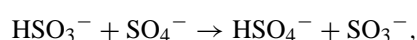
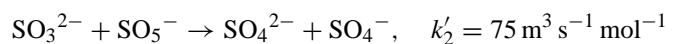
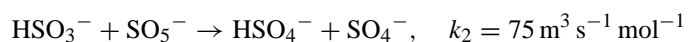
$$k = 9.6 \times 10^6 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$



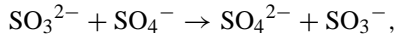
$$k' = 9.6 \times 10^6 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$



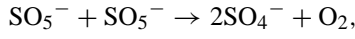
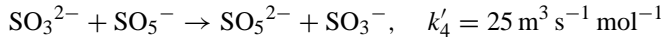
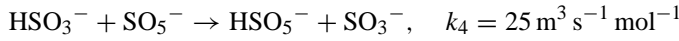
$$k_1 = 1.5 \times 10^6 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$



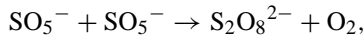
$$k_3 = 2.0 \times 10^6 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$



$$k'_3 = 2.0 \times 10^6 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$

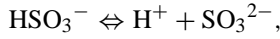
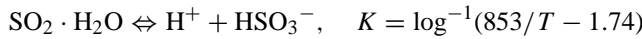


$$k_5 = 6.0 \times 10^5 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$



$$k_7 = 1.4 \times 10^5 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1}$$

Besides, the following ionization equilibriums also hold [5]:



$$K' = \log^{-1}(621.9/T - 6.278)$$

### 3. Kinetic equations

Suppose that the process reaches its steady state so that all the unknowns are independent of time  $t$ . Consider a thin sheet of a height  $\Delta y$  of the reactor with the gas and liquid in it (Fig. 1). With the aid of the radial electric wind only radial mass transfer from the gas to the liquid is significant and taken into account. In that case, the kinetic equations can be treated as a set of algebraic equations and established as follows [1]:

$$\begin{aligned} \text{OH}^- : \quad & kC_{\text{OH}}C_{\text{HSO}_3^-} + k'C_{\text{OH}}C_{\text{SO}_3^{2-}} \\ & = qG(\text{OH})\sqrt{\theta D\tau_{\text{OH}}/t_{\text{res}}l} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{SO}_3^- : \quad & k_1C_{\text{SO}_3^-} - H_{\text{O}_2}P_{\text{O}_2} + (k_6 + k_{11})C_{\text{SO}_3^{2-}} \\ & = kC_{\text{OH}}C_{\text{HSO}_3^-} + k'C_{\text{OH}}C_{\text{SO}_3^{2-}} \\ & \quad + k_3C_{\text{SO}_4^-} - C_{\text{HSO}_3^-} + k'_3C_{\text{SO}_4^-} - C_{\text{SO}_3^{2-}} \\ & \quad + k_4C_{\text{SO}_5^-} - C_{\text{HSO}_3^-} + k'_4C_{\text{SO}_5^-} - C_{\text{SO}_3^{2-}} \end{aligned} \quad (2)$$

$$\begin{aligned} \text{SO}_5^- : \quad & (k_2 + k_4)C_{\text{HSO}_3^-} - C_{\text{SO}_5^-} + (k'_2 + k'_4)C_{\text{SO}_3^{2-}} - C_{\text{SO}_5^-} \\ & + (k_5 + k_7)C_{\text{SO}_5^{2-}} = k_1C_{\text{SO}_3^-} - H_{\text{O}_2}P_{\text{O}_2} \end{aligned} \quad (3)$$

$$\begin{aligned} \text{SO}_4^- : \quad & k_3C_{\text{SO}_4^-} - C_{\text{HSO}_3^-} + k'_3C_{\text{SO}_4^-} - C_{\text{SO}_3^{2-}} \\ & = k_2C_{\text{HSO}_3^-} - C_{\text{SO}_5^-} + k'_2C_{\text{SO}_3^{2-}} - C_{\text{SO}_5^-} \\ & \quad + k_5C_{\text{SO}_5^{2-}} \end{aligned} \quad (4)$$

Because the characteristic time of ionization of the dissolved  $\text{SO}_2$  is even shorter than those of the mass transfer and reac-

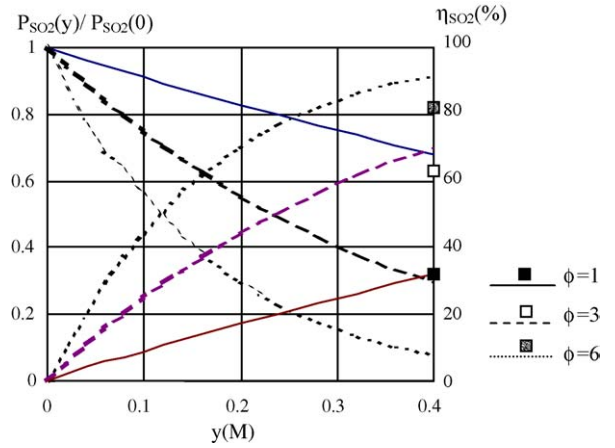


Fig. 2.  $P_{\text{SO}_2}$  and  $\eta_{\text{SO}_2}$  at different positions of  $y$  for different  $\phi$  ( $\text{pH}=4.0$ ,  $q=4 \text{ Wh/m}^3$ ). Symbols represent experimental values.

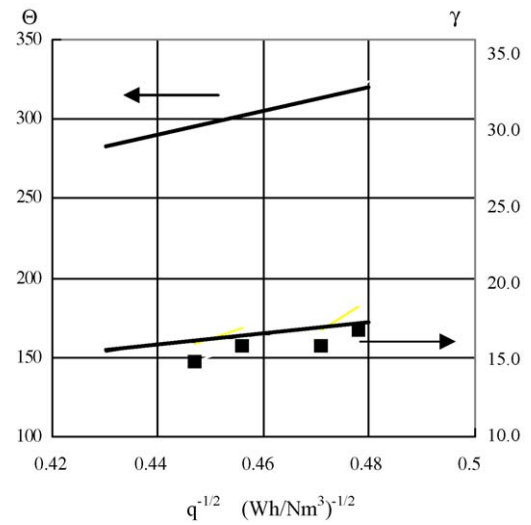


Fig. 3.  $\Theta$  and  $\gamma$  vs. the power density  $q$  ( $\text{pH}=4.28$ ,  $\phi=5.0$ ,  $t_{\text{res}}=10 \text{ s}$ ,  $\eta_{\text{SO}_2}=50\%$ ).

tions in the liquid, the dissolved  $\text{SO}_2$  will keep its ionization equilibrium, which is expressed as follows:

$$\text{HSO}_3^- : \quad C_{\text{HSO}_3^-} = KH_{\text{SO}_2}P_{\text{SO}_2}/C_{\text{H}^+} \quad (5)$$

$$\text{SO}_3^{2-} : \quad C_{\text{SO}_3^{2-}} = KK'H_{\text{SO}_2}P_{\text{SO}_2}/C_{\text{H}^+}^2 \quad (6)$$

In Eq. (1),  $\tau_{\text{OH}} = (3.0\text{--}6.0) \times 10^{-5} \text{ s}$  [6].

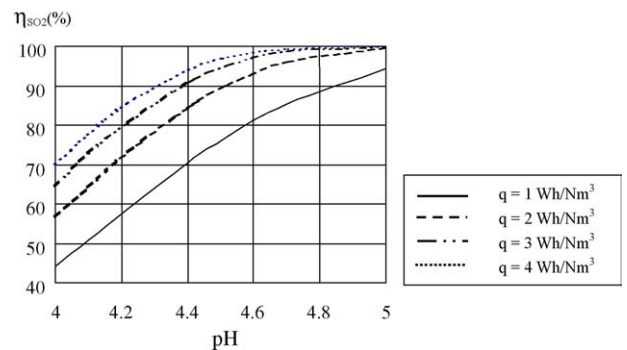


Fig. 4.  $\eta_{\text{SO}_2}$  vs.  $\text{pH}$  for different power injections.

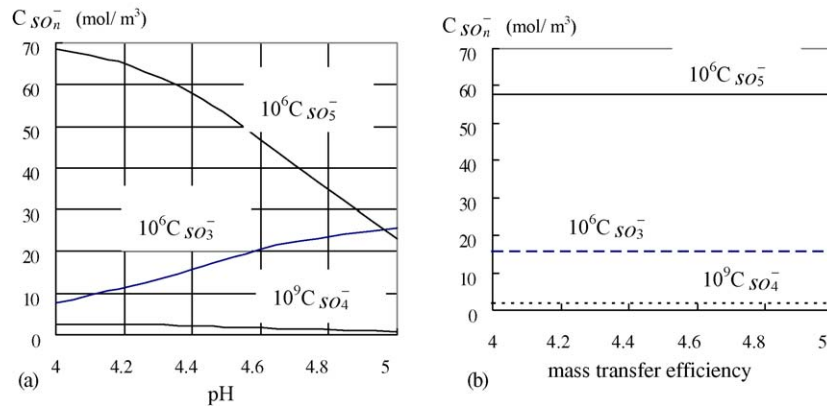


Fig. 5. (a)  $C_{SO_n^-}$  (in  $\text{mol m}^{-3}$ ) vs. pH ( $\phi = 3.0$ ,  $q = 4 \text{ Wh/N m}^3$ ,  $t_{\text{res}} = 10 \text{ s}$ , at  $P_{SO_2} = P_0/2$ ). (b)  $C_{SO_n^-}$  (in  $\text{mol m}^{-3}$ ) vs.  $\phi$  (pH = 4.4,  $q = 4 \text{ Wh/N m}^3$ ,  $t_{\text{res}} = 10 \text{ s}$ , at  $P_{SO_2} = P_0/2$ ).

Given the initial  $\text{SO}_2$  partial pressure  $P_{SO_2}(0)$  at the top end, solve Eqs. (1)–(6) by iteration for  $C_{OH}$ ,  $C_{SO_3^-}$ ,  $C_{SO_5^-}$ ,  $C_{SO_4^-}$ ,  $C_{HSO_3^-}$  and  $C_{SO_3^{2-}}$  at the  $n$ th sheet with  $\text{SO}_2$  partial pressure  $P_{SO_2}(n)$ . At the  $(n+1)$ th sheet, the partial pressure  $P_{SO_2}(n+1) = P_{SO_2}(n) - \zeta(P_{SO_2})(2\pi r l_0 \phi LRT/NQ)$ . Letting  $\text{SO}_2$  partial pressure at the lower end be  $P_{SO_2}(L)$ , the  $\text{SO}_2$  removal rate can be found to equal

$$\eta_{SO_2} = (P_{SO_2}(0) - P_{SO_2}(L))/P_{SO_2}(0) \quad (7)$$

The moles of the generated S(VI) per cubic meter per second  $\zeta(P_{SO_2})$  are:

$$\zeta(P_{SO_2}) = (k_2 C_{HSO_3^-} + k'_2 C_{SO_3^{2-}}) C_{SO_5^-} + (k_3 C_{HSO_3^-} + k'_3 C_{SO_3^{2-}}) C_{SO_4^-} \quad (8)$$

The chain length  $\Theta$  is

$$\Theta = \zeta(P_{SO_2}) / [(k_6 + k_{11}) C_{SO_3^-}^2 + k_7 C_{SO_5^-}^2] \quad (9)$$

The moles of the oxidized sulfite in the liquid phase per unit energy (named energy efficiency)  $G(\text{S(IV)})$  can be expressed as:  $G(\text{S(IV)}) = 2\pi r l_0 \phi h \zeta(P_{SO_2}) / W = 2l\phi \zeta(P_{SO_2}) / r q$ . Define  $\gamma(P_{SO_2}) = G(\text{S(IV)}) / G(\text{OH})$ , which expresses the generated sulfates per consumed OH radical by the discharges, and can be named apparent chain length.

All the solutions of  $C$ 's,  $\eta_{SO_2}$ ,  $\zeta(P_{SO_2})$ ,  $\Theta$ ,  $G(\text{S(IV)})$  and  $\gamma$  include parameters of energy density  $q$ , pH value, mass transfer efficiency factor  $\phi$ , residence time  $t_{\text{res}}$ , etc. so that their dependences upon the parameters can be obtained.

## 4. Results and discussions

### 4.1. Plots of $P_{SO_2}$ versus $y$

Fig. 2 shows  $P_{SO_2}$  and  $\eta_{SO_2}$  at different positions of  $y$  for different  $\phi$ . The desulfurization rates of experimental results for different  $\phi$  are from [1] and in agreement with the theory.

### 4.2. Chain length $\Theta$ and $\gamma$ versus the power density $q$

Fig. 3 shows the dependences of  $\Theta$  and  $\gamma$  upon the power density  $q$ .

Because  $\Theta$  and  $\gamma$  have a weak dependence upon the concentration of the sulfite ions within the range of our concern the initial  $\text{SO}_2$  partial pressure is chosen to be  $P_0 = 101.3 \text{ Pa}$  and the values of  $\Theta(P_{SO_2})$  are taken at  $P_{SO_2} = P_0/2$ . The experimental points around the  $\gamma - q^{-1/2}$  curve in Fig. 3 are selected from [1].

### 4.3. $\eta_{SO_2}$ versus pH of the liquid absorbent

Fig. 4 shows  $\eta_{SO_2}$  versus pH. It can be found that with increase of pH from 4.0 to 5.0 at  $q = 1 \text{ Wh/N m}^3$  the desulfurization rate increases from 44 to 94%. No additional energy injection is needed. Moreover pH  $\sim 5.0$  means a weak acidity of the absorbent and if ammonia is used for neutralization of the acid generated from the solved  $\text{SO}_2$  the  $\text{NH}_3$  slip can be controlled under environmental limit 5 ppm.

### 4.4. The concentrations of the ionic radicals

Fig. 5 shows the concentrations of the ionic radicals in the liquid versus pH (Fig. 5a) and  $\phi$  (Fig. 5b) for a given energy consumption  $q$  at  $P_{SO_2} = P_0/2$ . It is found that the concentrations of the ionic radicals have a weak dependence upon pH for given  $q$  and are constants for different  $\phi$ . That means that without any increase of energy input the oxidation can be promoted when the mass transfer efficiency factor  $\phi$  is increased or say the inner surface of the reactor is made appropriately porous. Besides, the total effective concentration of the ionic radicals under the conditions of the corona discharges is about 70 times of that in the experiments [7] with natural radicals in air so that the absorbed  $\text{SO}_2$  can be oxidized by over 99% in our case.

## 5. Conclusions

Through the model analysis above it is found that under the conditions of given energy injection of streamer plasmas the flue gas desulfurization rate can be remarkably increased when

the pH value of the liquid absorbent is appropriately adjusted and inner surface of the wet plasma reactor is appropriately porous. The energy consumption can be reduced to lower than 2–4 Wh/N m<sup>3</sup>, which is acceptable for industrial application.

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