A semi-wet technological process for flue gas desulfurization by corona discharges at an industrial scale

Keping Yan [a], Ruinian Li [a,*], Tianle Zhu [a], Hongdi Zhang [a], Xiaotu Hu [b],
Xuedong Jiang [b], Hui Liang [b], Ruichang Qiu [b], Yi Wang [b]

[a] *Guang Dong J-Tech Science Development Co. Ltd, China*
[b] *Beijing Jiaotong University, China*

Abstract

An industry-scale semi-wet technological process for flue gas desulfurization by corona discharges is recommended. Its characteristics are: (1) it uses an ac/dc power supply to generate uniformly distributed streamer plasmas; (2) it uses a partitioned wet reactor system in which SO_2 in the flue gas is absorbed with ammonia water in its thermal chemical reaction stage and the generated solution is repeatedly sprayed and transferred at an appropriate flow rate to the successive plasma reaction stage under the conditions of keeping liquid flow in balance. In the plasma stage, SO_2 absorption by the liquid is enhanced by the electric wind and the sulfites in the solution experiences plasma oxidization; (3) drying up the end liquid to produce powder-typed byproduct and discharging the end gas after heat exchange with the hot gas at the inlet. Through a pilot test of 12,000 Nm^3/h capacity of flue gas with an initial SO_2 concentration of about 500 ppm, results of desulfurization rate >95%, energy consumption in the reactor 1.8 Wh/Nm^3, ammonia slip less than 5 ppm and qualified fertilizer byproduct are obtained.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Streamer; Flue gas desulfurization; Semi-wet technological process; ac/dc power supply; Partitioned wet reactor

1. Introduction

Since the effects of $DeSO_2$ and $DeNO_x$ by non-thermal plasmas were discovered in 1970s [1] a good many researches were carried out in order to develop a practical technique acceptable to industry [2–6]. In 1980s Masuda et al. [7,8] discovered that a pulsate streamer corona also has effects of $DeSO_2$ and $DeNO_x$. At that time it had advantages in a good many aspects such as simultaneous removal of SO_2 and NO_x, simplicity of the dry process, no need to reheat the end gas in general, directly discharging the end gas and no production of any other wastes but useful fertilizer. Under these situations a Committee sponsored by the Japan Ministry of International Trade and Industry concluded that the technique of non-thermal plasma flue gas desulfurization and denitrification is technically the most simple and feasible as the next generation technology to be developed [9]. Since then various test schemes for developing this technique were carried out [10–19]. A pilot test with narrow pulsed high voltage to gener-

ate streamer plasma supported by ENEL Italy [11] obtained a result of acceptable $DeSO_2$ rate at an energy cost of 5 Wh/Nm^3. In the test, H_2O_2 was used to control the ammonia slip. In 2001, Zhao [13] built a pilot rig for flue gas $DeSO_2$ with narrow pulsate high voltage corona. The flow rate of the treated gas was 20,000 Nm^3/h. Under the conditions of temperature 65–70 °C, water vapor mole fraction of 10% and stoichiometric ratio of ammonia to SO_2 of 1:1, the $DeSO_2$ rate reached over 85% with a residence time of 6 s and energy cost of less than 5 Wh/Nm^3. The narrow pulsate high voltage power supply used had a front edge less than 100 ns, repetition rate: 50–200 pps, peak voltage: 100–150 kV and power output: 50–100 kW. The solid byproduct was collected with a steel brush electrostatic precipitator. In 2003, Kim et al. [14] reported results of a pilot test of a dry method flue gas $DeSO_2$ and $DeNO_x$ with narrow pulsate high voltage corona in DOOSAN, Korea. The pulse power supply was a magnetic pulse compressor with a power of 30 kW, pulse width 500 ns, peak voltage 100–130 kV, repetition rate: 300 pps and maintenance interval 3×10^9 pulses. The capacity of the treated gas was 1800 Nm^3/h. After the plasma treatment about 294 ppm of SO_2 was removed from the initial concentration 300 ppm. The ammonia slip was 26 ppm. $DeNO_x$ rate was

* Corresponding author.
E-mail address: liruinian@vip.sina.com (R. Li).

12% (no CH$_4$ injection) and 54% (with 200 ppm CH$_4$ injection) at initial concentrations of 245 and 312 ppm, respectively. Currently a system with a capacity of 35,000 Nm^3/h has been built up for further tests.

In fact when one tries to implement the electric discharge DeSO$_2$ technique industrially, pulse power supply is always the "bottleneck" of the technological process because high voltage, high speed and repetition rate switches have not been available in the world market to meet the demands of flue gas treatment industries in the respects of both price and techniques. Moreover, there are still a lot of problems to be resolved in building a technological process, such as high energy cost, the solid byproducts sticking to the walls of the plasma reactor and too high an ammonia slip from the end gas.

Along with the experimental development, exploration of the mechanism of DeSO$_2$ by plasmas was in progress. In the theoretical respects, for years past researches of plasma DeSO$_2$ were emphasized on the fundamental reactions in gas phase [20] and no sufficient theoretical results were approximated to the experiments. Paur and Jordan [21] discovered that with increase of water vapor in the gas the DeSO$_2$ rate had a remarkable rise, manifesting probable existence of two different mechanisms in his electron beam tests. Jordan [22] considered that 70–90% of SO$_2$ removal happens on the surfaces inside the plasma reactor and filter cake in his E-beam tests. In order to explain the oxidation processes of SO$_2$ dissolved in atmospheric droplets, Huie and Neta [23] provided a set of chain processes initiated by radical SO$_3$$^-$. Li et al. [24] adopted Huie's mechanism and considered the process should be divided into two steps: firstly SO$_2$ is transferred into liquid films formed on the surfaces of the solid inside the dry corona discharge reactor and secondly the radicals excited by the corona discharges oxidize the sulfites in the formed liquid films. By use of this concept and introduction of a mass transfer efficiency factor φ they made a semi-quantitative simulation about an electric discharge DeSO$_2$ reactor with some water vapor in the gas but no liquid injected around a temperature 75 °C. The agreement of the simulation with experiments provided evidence that the plasma assisted DeSO$_2$ process is mainly heterogeneous reactions [25]. Thus, it may be asked why not adopt a wet method instead of the dry one? Using a wet method might avoid byproduct sticking to the walls, but such an approach might be advantageous for heterogeneous reactions.

As for the DeSO$_2$ effect in wet electric discharge reactors, it has been investigated over many years. In 1971, Adachi [26] explored the DeSO$_2$ effect in a wet electrostatic precipitator. In 2000, Chao-Heng Tseng [27] also investigated the effects of both DeSO$_2$ and DeNO$_x$ in a wet ESP. Potapkin et al. [28] used the chain processes Huie provided and obtained theoretical results under the boundary conditions of a water spray in a E-beam reactor, compared with experimental results at 40–50 □ and made developments in heterogeneous reaction mechanism in DeSO$_2$ process. In 2001, Youhei et al. [29] used a piece of paper as a lining of a tubular electric discharge reactor. The lining was wetted with ammonium persulfate solution to enhance oxidation. At an initial concentration 400 ppm of SO$_2$ the DeSO$_2$ rate were 95% with an energy consumption ∼6 Wh/Nm^3. The byproduct was ammonium sulfate. In 2001, Kim et al. [30] also got similar results. In 2003, Mizuno [31] discussed the possibility to use wet plasma reactors for flue gas desulfurization.

Obviously all of these works have not reached the stage at which they could be used to develop an integrated technological process.

In this work an integrated technological process for electric discharge flue gas desulfurization, which may be accepted by industries, is recommended. Its characteristics are:

1. Using a dc power supply superimposed with an ac voltage to generate well-distributed streamer plasma in industry-scaled reactors.
2. Using a partitioned wet plasma reactor system instead of the traditional dry ones to overcome the difficulties in stickiness of solid products to the walls and decrease the energy consumption by a large margin.
3. After the end solution is dried up qualified ammonium fertilizer is produced. The end gas is discharged to open air after its heat exchange with the entering hot gas.

2. The technological process and the test results

Fig. 1 shows a schematic diagram of the technological process for the flue gas desulfurization. After dust removal the flue gas with a dust concentration less than 100 mg/Nm^3 at a temperature about 150 °C enters a heat exchanger to elevate the temperature of the end gas of the wet reactor system from about 50 to 90 °C for its discharging through a chimney. Then the flue gas is introduced to a spray dryer to evaporate the end liquid and produce dry powder of ammonium sulfate. Meanwhile, the flue gas becomes moistened and cooled and then enters the thermal chemical stage in which ammonia water is sprayed to absorb the SO$_2$ from the gas. Over 80% of the total SO$_2$ is absorbed. The generated liquid is cycled and repeatedly sprayed in this stage. When the concentration of the absorbent liquid reaches about 3 mol the generated solution will be transferred to and sprayed in the successive plasma stage at such an appropriate quantity that the liquid flow in the reactor system is kept in balance. The flue gas with the most SO$_2$ removed is further desulfurized and the sulfites in the sprayed solution are oxidized by the streamer conna in the plasma stage. By keeping the liquid flow in balance in the solution at its end may reach about 3 mol in concentration.
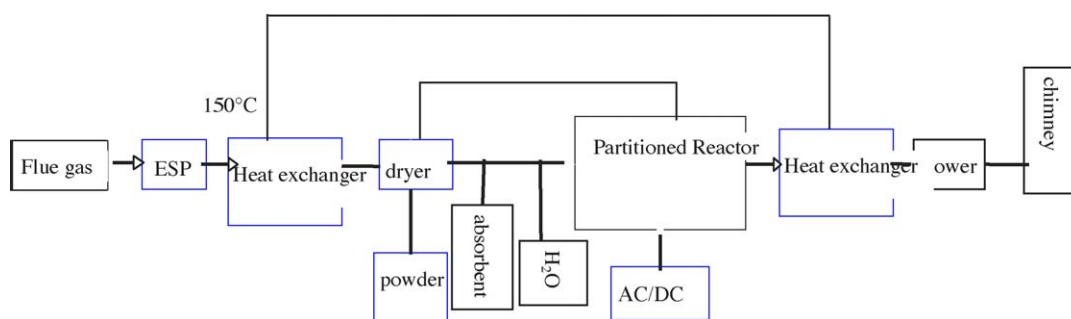
Fig. 1. Schematic diagram of the technological process of flue gas desulfurization.

After sufficient plasma treatment the percentage of the sulfates in the solution reaches over 90% (to be discussed in a separate issue). The end solution of appropriate quantity is taken out of the reactor, neutralized to pH 7.0 and dried up. In drying up the solution the generated water vapor and the volatized NH_3 and SO_2 is converged into the main pipeline of the system. Thus, the water consumption is equal to the saturated water vapor at the end of the reactor system minus the water vapor in the flue gas at the entrance of the process.

The characteristics of the semi-wet method lie in wet-typed reactor with liquid matter generated and dry powder byproduct generated after drying up the liquid from the reactor with the heat in the hot gas at the entrance of the process. No solid material is accumulated anywhere and the entire technological process can be kept steady and continuous (Table 1).

Fig. 2 shows the outward appearance of the 12,000 Nm^3/h streamer plasma flue gas desulfurization system.

Fig. 3 shows the temperatures at some points of the system through computing the material and heat balances (mathematical equations in Appendix A).

Table 2 gives the test results of the quality of the ammonium byproduct from the desulfurization process.

3. ac/dc power supply and the streamer generated

It was proved by experiments that the streamer mode of the gas discharge initiates remarkable chemical effects [32,33]. For the decades past, nano-second narrow pulse power supplies were developed for generating streamer corona [7–14]. However, the narrow pulse power supplies have never been accepted by the

Table 1
The results in a test of the semi-wet corona discharge flue gas desulfurization

Capacity of the flue gas flow (Nm^3/h)	6000
Residence time (s)	1.9
SO_2 concentration at the entrance (ppm)	572
SO_2 concentration at the exit (ppm)	21.6
Desulfurization rate (%)	96.2
Concentration of the generated liquid (mol)	4.66
$[NH_3]/2[SO_2]$	0.80
Ammonia concentration in the end gas (ppm)	3.5
Concentration of sulfite in the end liquid (mol)	2.43
Concentration of sulfate in the end liquid (mol)	2.23
Oxidation rate of generated sulfite in the process (%)	47.9
pH of the end liquid	5.2
Gas temperature at entrance of the wet reactor (°C)	70
Gas temperature at exit of the wet reactor (°C)	53
Gas temperature at the entrance of the chimney (°C)	85
dc voltage (kV)	48.4
ac peak–peak voltage (kV)	4.0
Power injected (kW)	1.7
Energy cost per unit volume of gas (Wh/Nm^3)	0.28
Mole oxidation energy cost (Wh/mol)	22.1

industries of flue gas desulfurization because no high voltage, high speed, long life and low price switches are available for flue gas cleaning industries.

Fig. 4 shows the different modes of gas discharges with dc positive high voltage and dc + ac between a point and a plate electrode. When a dc voltage is increased from 0 to V_c no corona occurs; from V_c to V_g appears a weak streamer, which has too low a power density to initiate significant chemical

Fig. 2. Outward appearance of the 12,000 Nm^3/h streamer plasma flue gas desulfurization system.

Table 2
The results of the quality of the dry ammonium byproduct

Items of the quality indices	Agricultural product (standard: GB 535—1995)		Byproduct
	First grade	Second grade	
Exterior	White crystal, no mechanical impurities	White crystal, no mechanical impurities	White crystal, no mechanical impurities
Ammonia (%)	≥ 21.0	≥ 20.8	21.25
Water content, H_2O (%)	≤ 0.2	≤ 0.1	2.49
Free acid, H_2SO_4 (%)	≤ 0.03	≤ 0.05	0.19

Fig. 3. The temperatures at the points of the system: (1) entrance of the dryer; (2) exit of the dryer; (3) entrance of the reactor; (4) exit of the reactor.
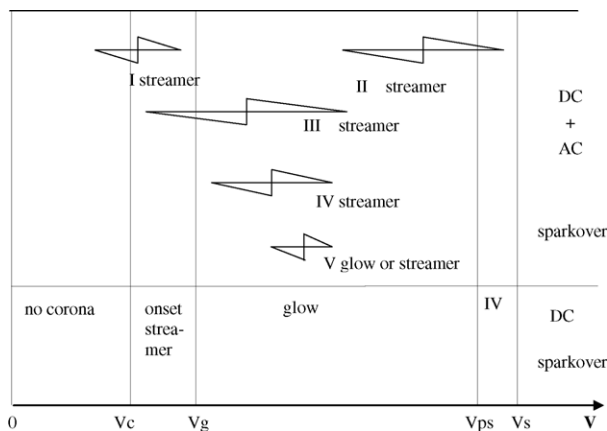

Fig. 4. dc + ac: I–IV streamer; V glow or streamer; dc: IV-prebreakdown streamer.
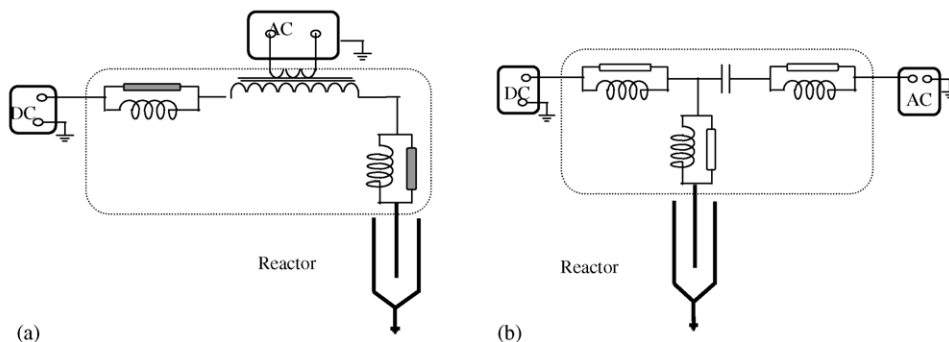
Table 3
The parameters of the ac/dc source

dc power (kW)	80
ac power (kVA)	80
dc voltage (kV)	0–60
Peak voltage of ac (kV)	20–80
ac frequency (kHz)	16–50
Efficiency of the source (%)	>80

effects. In a wide range of the voltage from V_g to V_{ps} the glow mode appears. Within the narrow range between V_{ps} and V_s, the mode is prebreakdown streamer. When the voltage is increased to V_s or higher, sparks occur. Streamer has a chemical effect higher than glow mode of the corona discharge by a 1000 times [32,33]. Therefore, only streamer discharges can be used for plasma reactors. In addition though the streamer can initiate chemical effects the range of voltage and variable gap length in which the streamer may be generated is too narrow to be used for industrial plasma reactors. In 1990s [32], it was discovered that when the dc voltage is superimposed an ac voltage with a rise rate and peak voltage V_p greater than $200 \, V/\mu s$ and $1 \, kV$, respectively, the Hermstein sheath in the positive glow can be destroyed and the corona may be transformed into streamer. A power supply with a dc superimposed an ac is called ac/dc source. ac/dc sources are even cheaper than nano-second pulsed power supplies and have even longer life. The successful fabrication of ac/dc source makes the large-scaled industrial plasma realizable. The parameters of the ac/dc source used in this experiment are specified in Table 3.

Fig. 5 shows two typical matching networks for superposition of dc and ac sources.

Fig. 6 shows the waveform of the ac used in our ac/dc source.

Fig. 7 shows the uniform distribution of the streamers with ac/dc power supply in a plasma reactor.

Fig. 5. (a) Direct coupling of dc and ac. (b) Capacitive coupling of dc and ac.
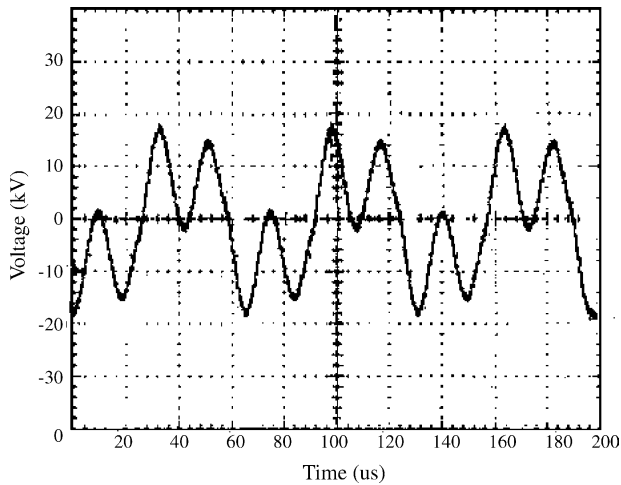
Fig. 6. 3 kV/48 kHz Wave of ac power supply output.
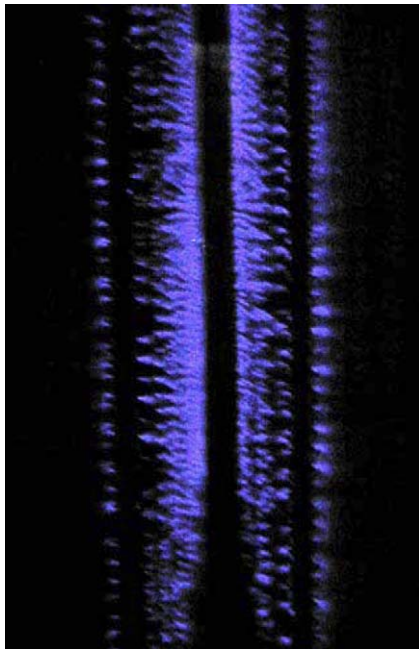

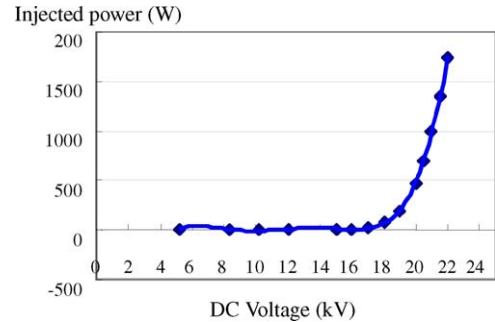Fig. 7. Streamers in the reactor.

Fig. 8. ac/dc power vs. the dc voltage (ac peak = 1.3 kV).

Fig. 8 shows the variation of the injected power (W) with the dc voltage when the peak voltage of the ac is 1.3 kV.

4. The partitioned wet plasma reactor

The reactor in the experiment is partitioned as a front thermal chemical stage and a successive plasma stage. There is no electric gas discharge in the thermal chemical stage, in which only ammonia water is sprayed for absorbing SO_2. Meanwhile, the generated solution is repeatedly sprayed in a circulating manner. When the concentration of the solution in the thermal chemical stage reaches about 3 mol/l an appropriate quantity of the solution is transferred to the next plasma stage under the conditions of balance of liquid flow. With the action of the plasmas the sulfites in the solution are oxidized and SO_2 in the gas phase is further absorbed in the liquid with enhancement of the electric gas discharge. In this case the sulfites in the plasma stage have been concentrated in the solution. Therefore, under the conditions of the same power injection the reaction speed is much higher than that in the wet reactors in which both thermal chemical and plasma reactions proceed in the same space. Partitioned wet reactors allow a remarkable decrease of energy consumption. Moreover, the solution produced in the reactors can be drawn from the reactor and treated outside with an external plasma reactor in open air or gas with even richer oxygen. The acidity of the solution in the plasma stage is controlled to an appropriate pH so as to control the ammonia slip below 5 ppm. Table 4 shows the data of the wet partitioned reactor in an operation.

Table 4
The effect of the main technological parameters on desulfurization rate

NH_3/SO_2					
$NH_3/2SO_2$	0.58	0.66	0.78	0.95	Entrance, SO_2 = 1020 ppm; dc/ac = 21 kV/1.3 kV; gas flow
η_{SO_2}(%)	72	92	98	100	rate = 3100 m^3/h; exit temperature = 60 ± 5 °C; liquid flow: Q_1 = 100 L/h (front) and Q_2 = 100 L/h (plasma stage)
SO_2 concentration at the entrance					
SO_2 (ppm)	490	678	797	987	NH_3/SO_2 = 1.32; dc/ac = 21 kV/1.3 kV; gas flow rate = 3100 m^3/h; exit
η_{SO_2}(%)	98	97	95	92	temperature = 60 ± 5 °C; liquid flow: Q_1 = 100 L/h (front) and Q_2 = 100 L/h (plasma stage)
Residence time					
τ (s)	3.77[a]	1.91[b]	1.20[c]		NH_3/SO_2 = 1.32; dc/ac = 21 kV/1.3 kV
Gas flow rate (m^3/h)	3100	6100	9700		
SO_2 (ppm)	987	493	524		
η_{SO_2}(%)	96	93	90		

[a] Q_1 = 100 L/h (front), Q_2 = 100 L/h (plasma stage).
[b] Q_1 = 150 L/h, Q_2 = 140 L/h.
[c] Q_1 = 150 L/h, Q_2 = 140 L/h.

5. Discussions

5.1. ac/dc power supply and the streamer it generates

As shown in Fig. 4, when the voltage increases from V_c into the range between V_g and V_{ps} the onset streamer becomes so intense that the electrons generated become more and more. With the free electron flying to the anode rapidly the heavy negative ions produced by electron capture of oxygen molecules are lumped in the vicinity of the anode tip to form so-called Hermstein sheath (Fig. 9) [34], which shields the field strength from the anode tip. In this case the streamer only exists within a small layer between the surface of the tip and Hermstein sheath. Outside this region only ionic current exists. As a result, glow mode initiates insignificant chemical effect [32,33].

However, it takes time to form an Hermstein sheath [35,36] through negative ion shift and diffusion. With some enough strong (e.g. an ac $V_p > 1$ kV) and speedy-changing (e.g. $dV/dt > 200$ V/μs) interference to the ion lumping the streamer may stretch out and into a large space between the two electrodes [34–37]. That is, the reason why ac/dc generates streamer corona. The streamer corona generated with ac/dc power supply is different from that with high voltage nano-second short pulsate power supply. The propagation speed of a streamer is about 2×10^5 to 2×10^6 m/s, which is a weakly increasing function of the voltage [34]. In general plasma reactors the discharge gap is about 10 cm. The transition time of the streamers through the gap should be less than the order of 100 ns. That is, the ultimate limit to pulse width of any high voltage short pulse power supply. But the peak voltage can be high so long as the voltage is dropped down before the streamer reaches the cathode. The voltage wave is transmitted along the line at a speed about 0.2 m/ns. To spread the voltage over a corona wire with a length 4 m, only a period of 20 ns is needed. In addition, the voltage is so high that the time lag of the streamers is negligibly short [37]. It can be considered that the streamers are initiated simultaneously along the wires. Therefore, this kind of streamer can be called "synchronous streamer". However, when ac/dc power supply is used the duration of each pulse is too long to avoid the streamer propagation to the cathode if the peak voltage is high. Under these conditions the only way is to keep the peak voltage lower than v_0 times the electrode gap length, where v_0 is the voltage decrease in streamer channel per unit length. In this case the peak voltage of ac/dc power should be low and the
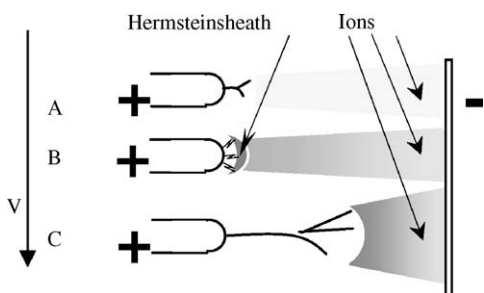

Fig. 9. (A) Onset streamer, (B) Hermstein glow and (C) prebreakdown streamer.
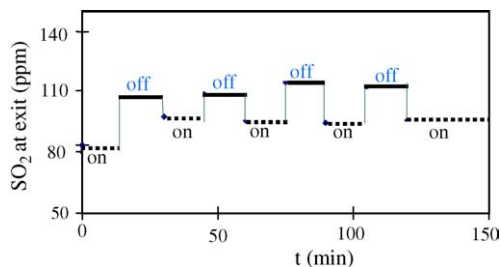

Fig. 10. Removal of SO_2 by electric gas dicharge. dc/ac = 21 kV/1.3 kV; power = 442 W; NH_3/SO_2 = 1.08; gas flow rate = 6100 m^3/h; Q_1 = 150 L/h and Q_2 = 50 L/h.

streamer initiation will be randomly distributed with in a longer interval of time lag.
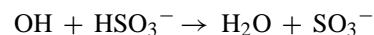
This streamer can be called random streamer. Owing to the long duration of the pulse the ionic current occupies 20% of the total current.

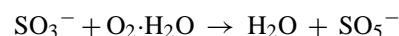### 5.2. Partitioned wet plasma reactor and G–L heterogeneous plasma reactor

The reactions in the thermal chemical stage have no difference from those of a traditional ammonia water process for SO_2 absorption from flue gas [38]. In the successive plasma stage SO_2 absorption by the sprayed solution is enhanced by the electric gas discharge [26,27,39,40]. Fig. 10 shows that when the gas discharge is switched on, the concentration of SO_2 in the gas decreases from 110 to 95 ppm. The mass transfer of SO_2 to the liquid is enhanced by about 10%. It is most important that the streamer plasma oxidizes the sulfites in the solution to sulfate by over 50% and denitrifies the flue gas and gives a comprehensive effect of controlling the ammonia slip to lower than 5 ppm. It is again proved that non-thermal plasma flue gas desulfurization mainly lies in the oxidation of the sulfites in the solution [24]. That is, the technical basis of the wet-type process for DeSO$_2$.

When a streamer as a filamentary discharge passes through air of 1 atm the field in the vicinity of the streamer head may reach a strength of 100–150 kV/cm, which can excite rich energy electrons of 12–16 eV [34]. The rich energy electrons can break bonds of molecules such as O_2, H_2O, N_2, generating radicals O, H, OH, N, etc., in which OH plays the most important role in oxidizing the sulfites [23–25]. In moist air (2.4% H_2O in volume, for example) within a volume of 15 mm^3 in the vicinity of the anode tip, the concentration of radical OH may reach 7×10^{14} cm^{-3} [41], which is 7 order of magnitude larger than that of the naturally existing OH [42,43]. That demonstrates why compressed air bubbling method takes even longer time to realize the oxidation than plasma catalytic method [43].
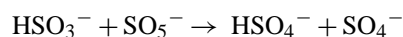
After OH is transferred into the solution the following chain reactions are initiated [23]:
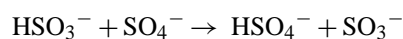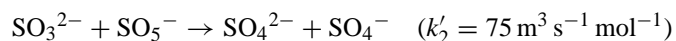
$$OH + HSO_3^- \rightarrow H_2O + SO_3^-$$

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

$$SO_3^- + O_2 \cdot H_2O \rightarrow H_2O + SO_5^-$$

$$(k_i = 1.5 \times 10^6 \, m^3 \, s^{-1} \, mol^{-1})$$

$$HSO_3^- + SO_5^- \rightarrow HSO_4^- + SO_4^-$$

$$(k_2 = 75\,\text{m}^3\,\text{s}^{-1}\,\text{mol}^{-1})$$

$$SO_3^{2-} + SO_5^- \rightarrow SO_4^{2-} + SO_4^- \quad (k_2' = 75\,\text{m}^3\,\text{s}^{-1}\,\text{mol}^{-1})$$

$$HSO_3^- + SO_4^- \rightarrow HSO_4^- + SO_3^-$$

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

$$HSO_3^- + SO_5^- \rightarrow HSO_5^- + SO_3^-$$

$$(k_4 = 25\,\text{m}^3\,\text{s}^{-1}\,\text{mol}^{-1})$$

$$SO_5^- + SO_5^- \rightarrow 2SO_4^- + O_2$$

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

$$SO_3^- + SO_3^- \rightarrow S_2O_6^{2-} \quad (k_6 = 1.0 \times 10^6\,\text{m}^3\,\text{s}^{-1}\,\text{mol}^{-1})$$

$$SO_5^- + SO_5^- \rightarrow S_2O_8^{2-} + O_2$$

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

If favorable conditions are created to improve the gas-to-liquid mass transfer the apparent chain length may reach over 15. When the sulfites in the solution are sufficiently oxidized the pH value of the solution can be controlled within the range of 4.8–5.3. Under these conditions the ammonia slip in the end gas can be controlled below 5 ppm.

As for the concentration effects on the oxidation of the sulfites in the solution there are two kinds of chemical actions with contrary effects. According to the law of mass reaction the reaction speed increases with increase of the concentration on one hand. On the other hand with increase of the concentration the solubility of oxygen decreases and the radical self-recombination speed increases, leading to slowing down the oxidation speed and increasing the energy consumption [44–47]. Under the conditions of using high concentration OH radicals excited with streamer plasmas generated by the ac/dc power supply an oxidation speed with industrial practical value can be achieved at a concentration of over 3 mol.

6. Conclusions

Using ac/dc power source well-distributed streamer plasmas can be generated in industrial scale reactors. Using wet streamer plasma reactors divided into thermal chemical reaction regions and plasma reaction regions, energy consumption is remarkably decreased and the problems due to the sticky byproducts are resolved. By combination of the two techniques an industry scale semi-wet technological process for flue gas desulfurization by corona discharges was implemented. Through a pilot test with a flue gas capacity of 12,000 Nm^3/h (normal cubic metre per hour) at an initial SO$_2$ concentration of ~500 ppm, the desulfurization rate is over 95% with an energy consumption of 1.8 Wh/Nm^3, ammonia slip less than 5 ppm and the byproduct is a qualified fertilizer.

Acknowledgements

Appendix A. Balance equations of mass and heat

(1) Fundamental chemical and physical data:

A_{H_2O} initial volumetric percentage of water vapor in the flue gas (%)

A_{N_2} volumetric percentage of N$_2$ in the flue gas (%) excluding water vapor

A_{O_2} volumetric percentage of O$_2$ in the flue gas (%) excluding water vapor

A_{CO_2} volumetric percentage of CO$_2$ in the flue gas (%) excluding water vapor

$A_{N_2} + A_{O_2} + A_{CO_2} = 1$

$B_{N_2} = 0.251$ (cal/g °C)   specific heat of N$_2$

$B_{O_2} = 0.291$ (cal/g °C)   specific heat of O$_2$

$B_{CO_2} = 0.208$ (cal/g °C)   specific heat of CO$_2$

$B_{H_2O} = 0.464$ (cal/g °C)   specific heat of H$_2$O (gas)

$B_{YAN} = A_{N_2}B_{N_2} + A_{O_2}B_{O_2} + A_{CO_2}B_{CO_2}$

$B_{AIR} = 0.79B_{N_2} + 0.21B_{O_2} = 0.244$ (cal/g °C)

$M_{YAN} = 28A_{N_2} + 32A_{O_2} + 44A_{CO_2}$

$M_{AIR} = 28 \times 0.79 + 32 \times 0.21 = 28.8$ (g/mol)

Evaporation heat of water   570 (cal/g)

$H(t)$ partial pressure of water vapor (mmHg)

t temperature (°C)

(2) Parameters of environment:

t_{hj} atmospheric temperature (°C)

v_3 relative humidity of atmosphere

(3) Technological parameters:

U volumetric flow rate at the entrance (Nm^3/h)

S_0 SO$_2$ initial concentration (ppm)

η_{SO_2} desulfurization rate (%)

W power of the electric discharge in the gas (kW)

(4) Characteristic parameters of the installations:

t_{hy} temperature of the trough of the generated liquid (°C)

χ_{gan} heat dissipation coefficient of the dryer (cal/h °C)

χ_h heat dissipation coefficient of the thermal chemical stage (cal/h °C)

χ_r heat dissipation coefficient of the reactor (cal/h °C)

U_1 volumetric flow rate of the gas carried by the liquid spray (Nm^3/h)

U_2 the flow rate of the gas for protection of the insulators (Nm^3/h)

(5) Control parameters of the technological process:

T_{CHU} the temperature at the exit of the dryer, no less than 80 °C

β byproduct recovery rate of the dryer (%)

α concentration of the end liquid/concentration of saturation

γ $\alpha\beta$

W_1 weight of water in the solution drawn from the end of the reactor per hour (kg/h) = $132.0US_0\eta_{SO_2}/(C\gamma \times 22.4E4)$ [C = solubility of ammonium sulfate (700 g/kg H_2O), η_{SO_2} desulfurization rate (%), molar weight of ammonium sulfate = 132 g/mol]

W_2 water injected per hour (kg/h) > $W_5 + W_1$

W_3 non-evaporated portion of the ijected water (kg/h) = $W_5 + W_1$

W_4 flow rate of water in the circulated solution 对流液含水量 (kg/h)

W_5 evaporated water from the circulated solution per hour (kg/h) = $W_3 - W_1$

Six unknowns:

v_1 relative humidity of the gas at the exit of the dryer

T_{RU} temperature of the flue gas at the entrance of the dryer

v_2 the relative humidity of the gas after water is injected

T_f temperature at the entrance of the reactor (°C)

T_{fw} temperature at the exit of the reactor (°C)

v_{fw} relative humidity of the gas at the exit of the reactor

Six equations:

1. Water balance of the dryer:

$$A_{H_2O}U(18/22.4) + W_1$$
$$= v_1(H(t_{chu})/760)(U(18/22.4) + W_1)$$

(the injected water W_1 is fully evaporated)

2. Heat balance of the dryer:

$$\left(\frac{(1 - A_{H_2O})U \times 10^3}{22.4}M_{YAN}B_{YAN}\right.$$
$$\left. + \frac{A_{H_2O}U}{22.4}18 \times 10^3 B_{H_2O}\right)(t_{RU} - t_{CHU})$$
$$= \chi_{GAN}[0.5(t_{RU} + t_{CHU}) - t_{hj}]$$
$$+ W_1 \times 10^3[570 + 1 \times (t_{CHU} - t_{hj})]$$

3. Water balance of the thermal chemical stage:

$$A_{H_2O}U\frac{18}{22.4} + W_1 + W_2 - W_3$$
$$= \frac{v_2 H(t_f)}{760}\left(U\frac{18}{22.4} + W_1 + W_2 - W_3\right)$$

(the injected water W_2 is partly evaporated)

4. Heat balance of the thermal chemical stage:

$$\left(\frac{(1 - A_{H_2O})U \times 10^3}{22.4}M_{YAN}B_{YAN}\right.$$
$$\left. + \frac{A_{H_2O}U}{22.4}18 \times 10^3 B_{H_2O}\right)(t_{CHU} - t_f)$$
$$= \chi_h[0.5(t_{CHU} + t_f) - t_{hj}]$$
$$+ (W_2 - W_3) \times 570 \times 10^3 + W_2 \times 10^3(t_f - t_{hj})$$

5. Water balance of the reactor:

$$A_{H_2O}U\frac{18}{22.4} + W_1 + W_2 - W_3 + W_5$$
$$+ \frac{v_3 H(t_{hj}) \times 18}{760 \times 22.4}(U_1 + U_2) = \frac{v_{fw}H(t_{fw})}{760}$$
$$\times \left(\frac{18}{22.4}(U + U_1 + U_2) + W_1 + W_2 - W_3 + W_5\right)$$

6. Heat balance of the reactor:

$$\left(\frac{(1 - A_{H_2O})U \times 10^3}{22.4}M_{YAN}B_{YAN} + \frac{A_{H_2O}U}{22.4}18\right.$$
$$\left. \times 10^3 B_{H_2O} + (W_1 + W_2 - W_3) \times 10^3 B_{H_2O}\right)(t_f - t_{fw})$$
$$+ 8.61 \times 10^5 W = \chi_f[0.5(t_f + t_{fw}) - t_{hj}]$$
$$+ W_4 \times 10^3[0.5(t_f + t_{fw}) - t_{hj}]$$
$$+ \left(\frac{(760 - v_3 H(t_{hj}))(U_1 + U_2) \times 10^3}{760 \times 22.4}M_{AIR}B_{AIR}\right.$$
$$\left. + \frac{v_3 H(t_{hj})}{760 \times 22.4}18 \times 10^3(U_1 + U_2)B_{H_2O}\right)(t_{fw} - t_{hj})$$

References

[1] K. Kawamura, et al., Flue gas treatment by electron beam irradiation, J. Atomic Energy Soc. Jpn. 20 (1978) 359–367.

[2] K. Kawamura, et al., Pilot plant experiment of NO_x and SO_2 removal from exhaust gases by electron beam irradiation, Radiat. Phys. Chem. 13 (1979) 5–12.

[3] N.W. Frank, et al., Design notes on testing conducted during the period of June 1985—September 1986 on the process demonstration unit at Indianapolis, Indiana, Electron Beam Process. Combust. Gases IAEA-TECDOC-428 (1987) 97–118.

[4] J.C. Person, D.O. Ham, Removal of SO_2 and NO_x from stack gases by electron beam irradiation, Radiat. Phys. Chem. 31 (1–3) (1988) 1–8 (Int. J. Radiat. Appl. Instrum. Part C).

[5] S. Jordan, Simultaneous $DeSO_x$ and $DeNO_x$ of flue gases in the agate pilot plant, Electron Beam Process. Combust. Gases IAEA-TECDOC-428 (1987) 135–150.

[6] F. Busi, et al., Radiation induced NO_x/SO_2 emission control for industrial and power plants flue gas, Radiat. Phys. Chem. 31 (1–3) (1988) 101–108 (Int. J. Radiat. Appl. Instrum. Part C).

[7] S. Masuda, et al., Control of NO_x by positive and negative pulsed corona discharges, in: Proceedings of the IEEE/IAS Annual Conference, Denver, 1986.

[8] A. Mizuno, et al., A method for the removal of sulphur dioxide from exhaust gas utilizing pulsed streamer corona for electron energization, IEEE Trans. Ind. Appl. IA–22 (1986) 516–521.

[9] S. Masuda, Report on novel dry $DeNO_x/DeSO_x$ technology for cleaning combustion gases from utility thermal power plant boilers, in: B.M. Penetrante, S.E. Schultheis (Eds.), Non-thermal Plasma Techniques for Pollution Control: Part B, Springer-Verlag, Berlin, 1993.

[10] L. Civitano, G. Dinilli, M. Rea, Removal of NO_x and So_x from combustion gasses by means of corona energization, in: Proceedings of the Third International Conference on Gas Discharges and their Applications, Venezia, 1987, pp. 19–23.

[11] L. Civitano, E. Sani, $DeNO_x$ and $DeSO_x$ process by gas energization, in: M. Capitelli, C. Gorse (Eds.), Plasma Technology: Fundamental and Applications, Plenum Press, 1987, pp. 153–166.

[12] G. Dinelli, L. Civitano, M. Rea, Industrial experiments on pulse corona simultaneous removal of NO_x and SO_2 from flue gas by means of impulse streamer corona, IEEE Trans. IAS 25 (1990) 535–541.

[13] J. Zhao, A pilot rig for flue gas De-SO_2 and De-NO_x by narrow pulsate high voltage corona, Electrostatic Precipitation Air Cleaning 7 (1) (2001) 4–7 (in Chinese).

[14] Y. Kim, et al., Development of demonstration plant using non-thermal plasma process to remove SO_2 and NO_x from flue gas, J. Adv. Oxid. Technol. 6 (1) (2003) 35–40.

[15] Y.H. Song, Y.H. Shin, Y.S. Choi, et al., An industrial-scale experiment of Pulse Corona process for removing SO_2 and NO_x from combustion flue gas, J. Adv. Oxid. Technol. 2 (2) (1997) 268–273.

[16] J.M. Rasmussen, High power duration pulse generator for SO_x and NO_x removal, in: Proceedings of the IEEE Annual Meeting on Industrial Applications, 1989, pp. 2180–2184.

[17] L.M. Zhou, E.M. van Veldhuizen, Medium-scale experiments on $DeNO/DeSO_2$ from flue gas by pulsed corona discharge, EUT-Report 96-E-302, December 1996, pp. 1–32, ISBN 90-6144-302-4.

[18] Y. Wu, J. Li, N. Wang, G. Li, Industrial experiments on desulfurization of flue gases by pulsed corona induced plasma chemical process, J. Electrostatics 57 (2003) 233–241.

[19] S. Hosokawa, K. Sonoyama, T. Yamamoto, PPCP pilot plant experiments for decomposition of dioxins, in: Proceedings of the Third International Symposium on Non-thermal Plasma Technology for Pollution Control, Korea, April 23–27, 2001, pp. 153–158.

[20] H. Matzing, Chemical kinetics of flue gas cleaning by irradiation with electrons, in: S.A. Rice, I. Prigogine (Eds.), Advances in Chemical Physics, vol. LXXX, John Wiley, New York, 1991, pp. 315–402.

[21] H.R. Paur, S. Jordan, Aerosol formation in electron beam dry scrubbing process, Radiat. Phys. Chem. 31 (1–3) (1988) 9–13.

[22] S. Jordan, On the state of the ART of flue gas cleaning by irradiation with fast electrons, Radiat. Phys. Chem. 35 (1–3) (1990) 409–415.

[23] R.H. Huie, P. Neta, Rate constants for some oxidations of S(IV) by radicals in aqueous solutions, Atmos. Environ. 21 (8) (1987) 1743–1747.

[24] R. Li, et al., Heterogeneous reactions in non-thermal plasma flue gas desulfurization, Chem. Eng. Sci. 53 (8) (1998) 1529–1540.

[25] R. Li, X. Liu, Main fundamental gas reactions in denitrification and desulfurization from flue gas by nonthermal plasmas, Chem. Eng. Sci. 55 (2000) 2491–2506.

[26] T. Adachi, Experimental discussion on removal function of SO_2 from stack gas by a wet type electrostatic precipitator, IEEJ 97 (6) (1977) 521–528.

[27] Chao-Heng Tseng, Enhanced Pulsed Corona Method for the Removal of SO_2 and NO_x from Combustion Gas in a Wet Electrostatic Precipitator, PhD thesis, Department of Environmental Engineering, University of Cincinnati, 2000.

[28] B.V. Potapkin, M.A. Deminsky, A.A. Fridman, The effect of clusters and heterogeneous reactions on non-equilibrium plasma flue gas cleaning, NATO ASI Ser. G34(A) (1993) 91–106.

[29] K. Youhei, S. Keita, T. Kazunori, K. Shinji, M. Akira, Removal of SO_2 using a wet-type non-thermal plasma reactor, in: Proceedings of the IEEE/IAS Meeting Record, 2001, pp. 693–697.

[30] H.H. Kim, et al., The influence of reaction conditions on SO_2 oxidation in a discharge plasma reactor, IEEE Trans. Ind. Appl. 37 (2) (2001) 480–487.

[31] A. Mizuno, Industrial application of non-thermal plasma in gas cleaning, in: Proceedings of the 10th Conference on Electrostatic Precipitation and Second Conference on Desulfurization held in Guangzhou, China, November, 2003, p. 559.

[32] K. Yan, T. Yamamoto, S. Kanazawa, T. Ohkubo, Y. Nomoto, J.S. Chang, No removal characteristics of a corona radical shower system under dc and ac/dc superimposed operation, in: Proceedings of the Conference Record of IEEE/IAS Annual Meeting, October 12–16, 1998.

[33] K. Yan, T. Yamamoto, S. Kanazawa, No removal characteristics of a corona radical shower system under dc and ac/dc superimposed operations, IEEE Trans. Ind. Appl. 37 (5) (2001) 1499–1504.

[34] R.S. Sigmond, The residual streamer channel: return strokes and secondary streamers, J. Appl. Phys. 56 (5) (1984) 1335–1370.

[35] E.W. McDaniel, Collision Phenomena in Ionized Gases, Wiley, New York, 1964.

[36] R. Morrow, The theory of positive glow corona, J. Phys. D: Appl. Phys. 30 (1997) 3099–3114.

[37] J.M. Meek, J.D. Craggs (Eds.), Electrical Breakdown of Gases, Wiley, New York, 1978, pp. 345, 655.

[38] L. Ferrao (Ed.), Lentjes Bischoff ammonia water process for SO_2 absorption from flue gas, Chem. Eng. World 33 (11) (1998) 75–78.

[39] N. Vasishtha, A.V. Samashwar, Absorption characteristics of sulfur dioxide in water in the presence of a corona discharge, Ind. Eng. Chem. Res. 27 (1988) 1235–1241.

[40] E.P. Maximuk, M.K. Bologa, Some mechanisms of electric field influence on mass transfer processes in the gas–liquid system, J. Electrostatics 40/41 (1997) 663–668.

[41] R. Ono, T. Oda, Dynamics and density estimation of hydroxyl radicals in a pulsed corona discharge, J. Phys. D: Appl. Phys. 35 (2002) 2133–2138.

[42] X. Ren, et al., Measurement of radical OH concentration in atmosphere, Chin. Environ. Sci. 21 (2) (2001) 115–118.

[43] J. Zhou, W. Li, W. Xiao, Kinetics of heterogeneous oxidation of concentrated ammonium sulfite, Chem. Eng. Sci. 55 (2000) 5637–5641.

[44] P.H. Wine, et al., Kinetics of aqueous phase reactions of the SO_4^- radical with potential importance in cloud chemistry, J. Geophys. Res. 94 (D1) (1989) 1085–1094.

[45] J.H. Espenson, Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, New York, 1981, pp. 172–175.

[46] R.E. Huie, C.L. Clifton, Temperature dependence of the rate constants for reactions of the sulfate radical, SO_4^-, with anions, J. Phys. Chem. 94 (1990) 8561–8567.

[47] E. Narita, et al., Solubility of oxygen in aqueous electrolyte solutions, Hydrometallurgy 10 (1983) 21–37.