



Full Length Article

Plasma-enhanced SO₂ remediation in a humidified gas matrix: A potential strategy for the continued burning of high sulfur bunker fuel

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ABSTRACT

We report a substantial enhancement in the removal of gaseous SO₂ by discharging a transient nanosecond pulsed plasma in a water vapor-saturated gas mixture. With the plasma alone (i.e., “dry”), the SO₂ remediation is limited to approximately 15% reduction in SO₂ (i.e., ΔSO₂ = 65 ppm). In presence of water vapor, we observe 84% remediation (ΔSO₂ = 500 ppm) during plasma discharge due to the availability of OH radicals. Here, there is a synergistic effect of adding water vapor to the gas mixture in which the plasma excites highly reactive OH radical species that drive a two-step reaction process: SO₂ + OH → HSO₃ and the subsequent reaction of HSO₃ + OH → H₂SO₄, which precipitates out in the aqueous phase. The efficacy of this approach increases as we increase the temperature of the gas matrix, indicating the relatively low barriers of this reaction, which is consistent with the OH-driven reaction pathway, and it also increases with plasma density, thus demonstrating the scalability of this approach. Plasma emission spectroscopy as well as Raman scattering spectroscopy provide spectroscopic evidence of the OH radical species, further substantiating the OH reaction intermediate mechanism. This approach provides a promising mitigation strategy for the continued use of high sulfur fuels (i.e., bunker fuel).

Sulfur dioxide (SO₂) is a toxic gas produced as a by-product of the burning of fossil fuels containing sulfur compounds. These high sulfur-containing fuels are almost exclusively used by the international shipping industry, and the international Marine Organization (IMO) has set a global limit for sulfur in fuel oil used on board ships of 0.50% m/m (mass by mass) starting 1 January 2020. The previous global limit for sulfur content of ships' fuel oil was 3.5% (i.e., heavy fuel oil). Currently, heavy fuel oil (also known as “Bunker Fuel”) comprises 4% of every barrel of crude oil, which corresponds to 10,000 tons of sulfur emissions globally each day. The new 2020 global limit of 0.50% corresponds to an 85% reduction in SO₂, which we believe can be achieved with our plasma-based approach.

While many research groups (including our own) have demonstrated highly effective NO remediation using plasma-based processes [1–6], SO₂ treatment remains challenging. In diesel exhaust, this problem is exacerbated because of the presence of NO, which rapidly consumes a vast majority of the oxygen radicals in the plasma, via the reaction NO + O →

NO₂. As such, the NO remediation reaction serves as a competing reaction pathway, which rapidly consumes most of the plasma-generated radicals. While existing technologies exist for reducing NO_x efficiently (i.e., selective catalytic reduction (SCRs)), effective methods for removing SO₂ are still very much lacking. SO₂ wet scrubber technologies are limited by the low solubility of SO₂ in water, which is several orders of magnitude lower than the solubility of H₂SO₄. Therefore, one strategy for SO₂ remediation is to first convert SO₂ to H₂SO₄ and then capture in H₂O using a “wet scrubber” with nearly unity capture.

Yamamoto's group investigated a single-stage wet plasma reactor for the simultaneous removal of NO_x, SO_x, and particulates by flowing Na₂SO₃ and NaOH solutions along the inner wall of the reactor [7]. However, the reaction pathways and temperature dependences of these reactions remain poorly understood. While SO₂ is more soluble in water than CO₂, there are several equilibrium processes that occur between SO₂ and various hydrogenated and oxygenated species (e.g., HSO₃[−]). We have the following reactions/equilibria:

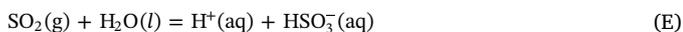
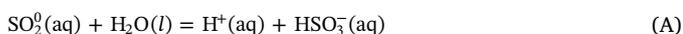
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Once equilibrium is reached with these back reactions, the remediation is limited, and no further SO_2 can be removed from the system. This plasma-based approach enables us to circumvent the standard $\text{SO}_2(\text{g})/\text{H}_2\text{SO}_4^0(\text{aq})$ equilibria, thus, enhancing the SO_2 remediation process.

In the work presented here, we demonstrate a method for improving SO_2 remediation using plasma discharge in a heated, plasma-driven reactor in the presence of water vapor. We present a systematic study of this reaction as a function of temperature and plasma density. A comparison of SO_2 reduction carried out under wet and dry conditions was performed in order further understand the synergistic roles of water vapor and plasma discharge. We also present spectroscopic evidence of the OH radicals, in order to substantiate the hypothetical OH-driven reaction pathway, which represents an important, short-lived reaction intermediate species.

1. Experimental details

In the work presented here, we utilize a transient pulsed plasma discharge in a coaxial reactor. As illustrated in Fig. 1, the plasma-based flow reactor consists of a 3 ft-long, 2 in.-diameter stainless steel cylindrical anode with a single-wire cathode center electrode. The plasma is produced using a TPS Model 20X pulse generator (Transient Plasma Systems, Inc.) operating at a peak voltage of 17 kV, pulse repetition rates up to 2000 Hz, and continuous powers up to 800 W. Here, the

plasma density is varied by adjusting the pulse repetition rate. A typical waveform produced by this pulse generator is plotted in Fig. 1b. While radio frequency (RF)-based plasma reactors have been investigated for remediation of diesel exhaust for several decades [8–14], the nanosecond pulsed plasma used here consumes far less energy in the creation of the plasma. The transient nature of the plasma necessitates that very little current is drawn in creating the plasma. That is, once the streamer is created, the applied field collapses before a substantial amount of current (and hence electric power) can flow. Because of its transient nature, this is a cold plasma, in which the electron energies are around 30 eV ($T = 10^5$ K), while the vibrational modes of the molecules remain at room temperature. These “hot” electrons enable new chemical pathways to be explored in the formation of energetic intermediate species that are otherwise not possible to make through standard equilibrium chemistry. At a peak voltage 17 kV, our system delivers a transient power of 4.76 MW. SO_2 concentrations were measured using a Horiba portable gas analyzer (model PGA-350) with a sample rate of 0.5 L/min after passing through a water knock out. This model detects SO_2 using non-dispersive infrared absorption with a measurement repeatability of $\pm 1\%$ relative to the full measurement scale of 1000 ppm or ± 10 ppmV absolute. Our synthetic gas mixture was prepared by mixing neat SO_2 gas with compressed dried air to a concentration of 500 ppm by volume. The flow rate of the synthetic gas mixture through the reactor was 4.75 slpm. Water vapor was injected into the reactor using an ultrasonic nozzle at a flow rate of 0.42 mL/min. This is a heated reactor, in which the sidewalls of the reactor are kept above 100 °C, meaning that all H_2O stays in the gas phase during the residence time in the reactor. The total reactor volume is 2.2 L resulting in residence times ranging from approximately 16–22 s. After exiting the heated reactor, the sample is transferred by a short (~18 in.) heated PTFE line to a borosilicate Greenburg-Smith type impinger with a straight stem (no bubbling plate) submerged in an ice bath. The design allows for the removal of moisture while minimizing negative bias

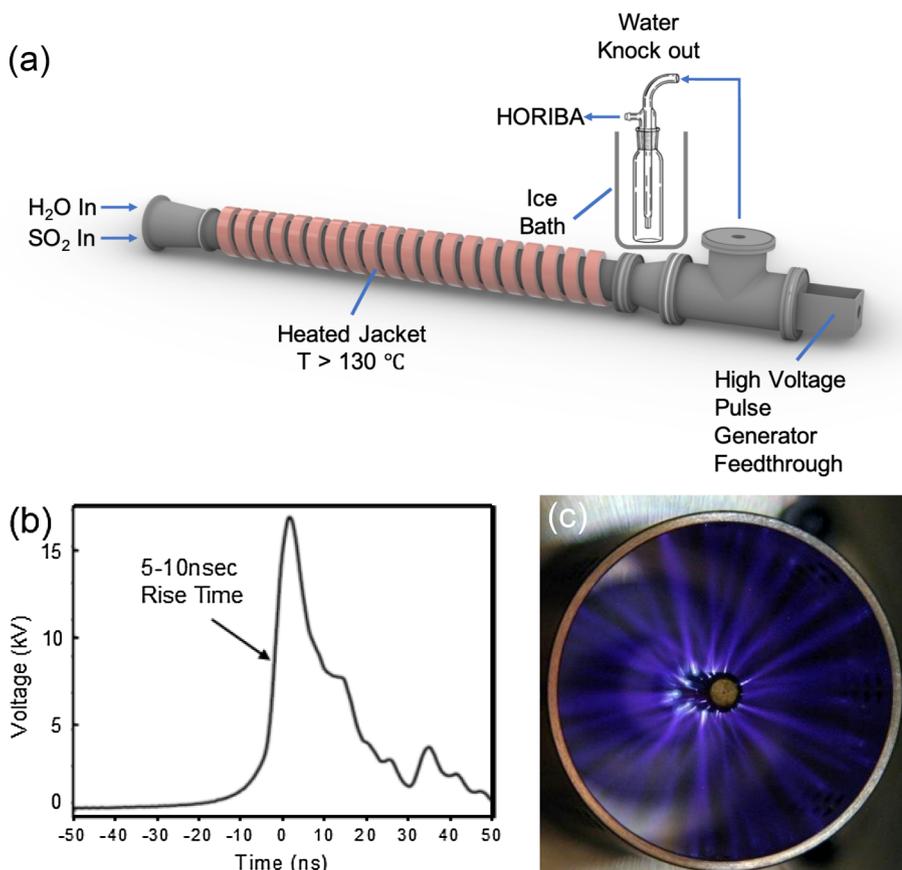


Fig. 1. (a) Schematic diagram of the experimental setup used to test the transient pulsed plasma reactor. (b) Typical output characteristics of nanosecond high voltage pulse generator (USC-patented technology). (c) Photograph of the transient plasma (hot electron, low-temperature plasma) formed by the high voltage nanosecond pulse.

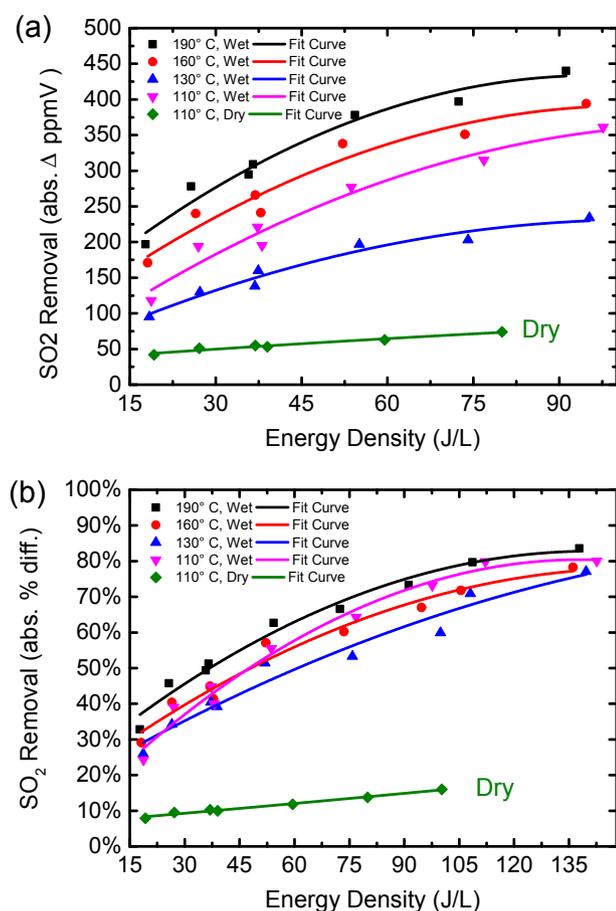


Fig. 2. Temperature dependent SO_2 remediation study on approximately 600 ppmV synthetic SO_2 in a humidified air matrix.

resulting from dissolved SO_2 by limiting the surface area where interaction may occur between condensed water and the gas sample. The condensation of sulfuric acid leading to corrosion in flue gas cleaning operations is a well-known phenomenon that is heavily dependent upon the composition of the flue gas matrix and the specific dynamic thermodynamic parameters of the cleaning system [15]. Both the gas composition and dynamic thermodynamic conditions experienced throughout the system result in difficulty estimating the acid dew point.

The experimental system used here mitigated the potential for sulfuric acid aerosol formation and condensation by operating at ambient pressures and minimizing system temperature differentials prior to moisture removal.

Fig. 2a shows a plot of the absolute SO_2 removal (in units of Δppm as measured by volume) brought about by the plasma discharge. As a comparison, we measure the removal efficacy in dry SO_2 in air (i.e., without water vapor injection). Here, we see that only about 65 ppm (or 15%) of the SO_2 is removed with plasma discharge and is largely independent of plasma density. This behavior reflects the limitation in the availability of OH radicals without the injection of water. That is, there are simply not enough OH radicals in the plasma to remediate all of the SO_2 and, therefore, much of the plasma's energy goes into generating oxygen radicals which drive the back reactions to SO_2 . Fig. 2a shows our results taken at moderate plasma densities (i.e., up to 100 J/L), and Fig. 2b shows results taken at high plasma densities (i.e., up to 145 J/L). Here, we observe a dramatic increase in the presence of water injection, yielding 84% (500 ppm) removal of SO_2 in the humidified gas matrix.

In order to substantiate our hypothesis that OH radicals drive the intermediate steps in this SO_2 remediation reaction, we performed *in situ* plasma emission spectroscopy of our nanosecond pulsed plasma discharge with water, which shows a clear peak around 927 nm, as shown in Fig. 3a [16]. These spectra were taken using a micro-spectrometer described in Fig. S1 of the Supporting Information. This feature is associated with charge neutral OH radicals, which correspond to highly chemically active, short lived species, as reported by Sato et al. [16]. These radical species produce several oxidizing agents, such as ozone and hydrogen peroxide that can be detected chemically [17–21]. This pulsed discharge approach has been utilized for water purification via the oxidation of volatile organic compounds (VOCs) [16,20–25]. Fig. 3b shows surface enhanced Raman scattering (SERS)-enhanced vibrational spectra of $\text{H}_2\text{O}/\text{SO}_2$ -plasma exposed Ag nanoparticles. Sharp peaks observed around 624 and 928 cm^{-1} are in agreement with SO_3^{2-} species, which correspond to the deprotonated HSO_3^- reaction intermediate [26–28]. These spectroscopic signatures provide further evidence of the OH-driven reaction pathway proposed for this water vapor-enhanced, plasma-driven process. This approach circumvents the standard $\text{SO}_2(\text{g})/\text{SO}_2(\text{aq})$ equilibria and overcome the relatively low solubility of SO_2 in water, which is several orders of magnitude lower than the solubility of H_2SO_4 . The H_2SO_4 can then be removed in H_2O with nearly unity capture and subsequently titrated, as is typical done in wet scrubbers.

This plasma-enhanced SO_2 remediation process may enable ships to burn high sulfur fuels while meeting the IMO SO_x 2020 emissions

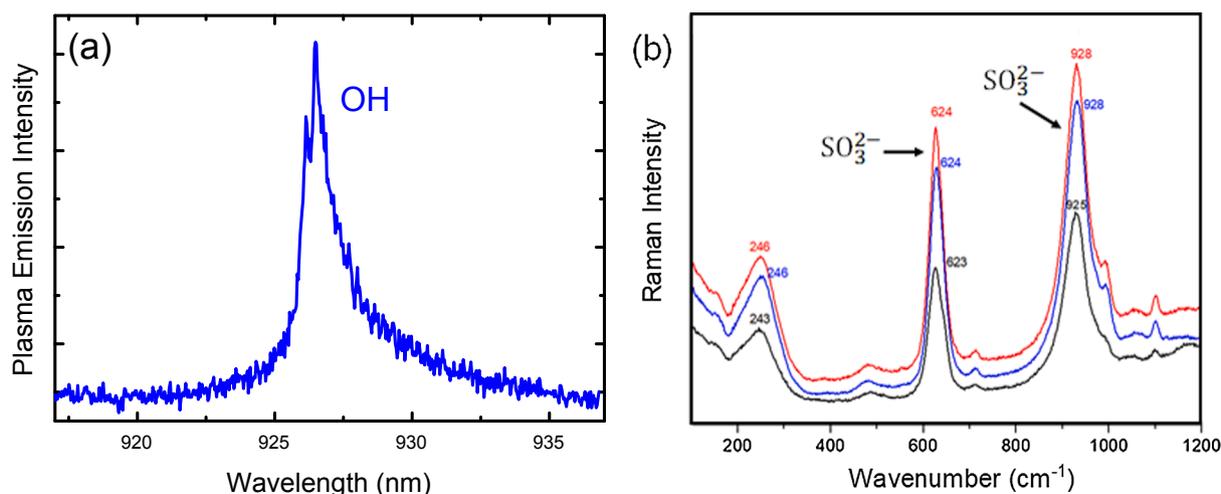


Fig. 3. (a) Plasma emission spectra of OH radicals observed from high voltage discharge in aqueous solution. (b) SERS-enhanced vibrational spectrum of SO_2 -plasma exposed Ag nanoparticles.

standards. The price of low sulfur bunker fuel (\$540 per metric ton) is typically 30–40% more expensive than that of high sulfur bunker fuel (\$400 per metric ton) [29,30]. For a typical ship burning 100 tons of fuel per day, this price differential equates to a cost savings of \$5M per year, providing a large economic incentive to implement this plasma-based technology.

The results presented here were carried out using compressed air. In actual flue gas, however, the elevated temperature and presence of other species including NO, NO₂ and particulate matter PM can play a significant role. On one hand, the higher temperatures will shorten radical lifetimes (e.g., atomic O, O₃, and OH), the presence of PM has been shown to increase NOx remediation by providing a surface that influences the reaction kinetics. In addition, the presence of NOx will also compete for the radicals generated by the plasma including atomic O and OH. However, efficient methods for removing NOx currently exist (e.g., diesel oxidation catalysts) and may be used in conjunction with the plasma-enhanced SOx scrubber demonstrated here.

In conclusion, we report the synergistic effect of discharging nanosecond pulsed plasma in a humidified SO₂ gas matrix. Here, a substantial enhancement in the remediation of gaseous SO₂ is produced beyond that achieved with the plasma discharge alone (i.e., “dry”) or with the water vapor alone (i.e., no plasma). Together, the water vapor-enhanced, plasma-driven process produces a 84% reduction in SO₂, whereas the dry, plasma-driven process only produces a 15% reduction in SO₂. Here, the main mechanism of SO₂ remediation reaction lies in the availability OH radicals, which drives the following reaction processes: SO₂ + OH → HSO₃ and HSO₃ + OH → H₂SO₄. Spectroscopic evidence of the short-lived, highly reactive OH radical is obtained through plasma emission spectroscopy and SERS-enhanced Raman spectroscopy. The SO₂ removal efficacy increases with increasing temperature, reflecting the relatively low barriers of this reaction, and it also increases with plasma density demonstrating the scalability of this approach.

CRedit authorship contribution statement

Christi Schroeder: Conceptualization, Methodology, Investigation, Validation, Writing - original draft, Writing - review & editing. **William Schroeder:** Conceptualization, Methodology, Investigation. **Sisi Yang:** Investigation, Data curation. **Haotian Shi:** Investigation, Data curation. **Alec Nystrom:** Methodology. **Sriram Subramanian:** Investigation, Methodology. **Shujin Li:** Investigation, Data curation. **Martin A. Gundersen:** Conceptualization. **Stephen B. Cronin:** Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: W.P. Schroeder, spouse of C. Schroeder, previously received research support from the TCC group through USC. W.P. Schroeder continues to serve in an advisory capacity as a paid consultant for the TCC group.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2020.117810>.

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