

SYSTEMS AND METHODS FOR PLASMA-BASED REMEDICATION OF SO_x AND NO_x

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application No. 62/816,589 filed March 11, 2019, U.S. Provisional Application No. 62/816,694 filed March 11, 2019, and U.S. Provisional Application No. 62/944,970 filed December 6, 2019, the contents of each of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] This invention relates to methods and systems for reducing the concentration of SO_x and/or NO_x in a gas stream.

BACKGROUND

[0003] All publications herein are incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference. The following description includes information that may be useful in understanding the present invention. It is not an admission that any of the information provided herein is prior art or relevant to the presently claimed invention, or that any publication specifically or implicitly referenced is prior art.

[0004] 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) from 1 January 2020. This will significantly reduce the amount of sulfur oxides emanating from ships and should have major health and environmental benefits for the world, particularly for populations living close to ports and coasts. The current global limit for sulfur content of ships' fuel oil is 3.50% (i.e., heavy fuel oil). The new 2020 global limit of 0.50% corresponds to a 7-fold reduction in SO_x, which can be achieved with our plasma-enhanced wet scrubber device. Without some form of sulfur remediation technology, these IMO standards will have a catastrophic impact on the petroleum industry by upsetting the supply-demand equilibrium.

[0005] Therefore, there is a need for methods and apparatus for SO_x and/or NO_x remediation. The embodiments of the present invention address that need.

SUMMARY OF THE INVENTION

[0006] The following embodiments and aspects thereof are described and illustrated in conjunction with systems, apparatus, articles of manufacture, compositions, and methods which are meant to be exemplary and illustrative, not limiting in scope.

[0007] In various embodiments, the present invention provides a system for plasma-based remediation, comprising: a flow reactor, wherein the flow reactor comprises an internal chamber and an electrode at least partially disposed within the internal chamber, the internal chamber being configured to be fluidly coupled to a gas source such that a gas from the gas source flows into the internal chamber of the flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof; a pulse generator electrically coupled to the electrode of the flow reactor, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas, the first chemical compound being converted to a second chemical compound in the plasma; and a water source fluidly coupled to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor to form [•]OH (hydroxyl radical) molecules from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, the [•]OH molecules reacting with the second chemical compound in the plasma so as to convert the second chemical compound into a water soluble chemical compound, and at least a second portion of the injected water removing the water soluble chemical compound from the flow reactor, thereby reducing the concentration of the first chemical compound in the gas. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, NO_x is NO. In some embodiments, the second chemical compound is NO₂. In some embodiments, the water soluble chemical compound is HNO₃. In some embodiments, SO_x is SO₂. In some embodiments, the second chemical compound is HSO₃. In some embodiments, the water soluble chemical compound is H₂SO₄. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some

embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both.

[0008] In various embodiments, the present invention provides a method for plasma-based remediation, comprising: receiving a gas from a gas source into an internal chamber of a flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof; delivering electric pulses to an electrode positioned in the internal chamber such that a plasma is formed from the gas, wherein the first chemical compound is converted to a second chemical compound in the plasma; injecting water into the internal chamber of the flow reactor in the presence of the plasma, wherein 'OH (hydroxyl radical) molecules are formed from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, and wherein the 'OH molecules react with the second chemical compound so as to convert the second chemical compound into a water soluble chemical compound; and removing at least a second portion of the injected water from the flow reactor, wherein the second portion of the injected water comprises the water soluble compound, thereby reducing the concentration of the first chemical compound in the gas. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, NO_x is NO. In some embodiments, the second chemical compound is NO₂. In some embodiments, the water soluble chemical compound is HNO₃. In some embodiments, SO_x is SO₂. In some embodiments, the second chemical compound is HSO₃. In some embodiments, the water soluble chemical compound is H₂SO₄. In some embodiments, the electric pulses are delivered by a pulse generator. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both.

[0009] In various embodiments, the present invention provides a plasma reactor for plasma-based remediation, comprising: a flow reactor comprising an internal chamber; a gas input port coupled to the flow reactor, the gas input port being configured to fluidly couple a gas source to the flow reactor such that a gas can flow into the internal chamber of the flow reactor; an electrode at least partially disposed within the internal chamber of the flow reactor; a pulse generator electrically coupled to the electrode, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas; a water inlet port coupled to the flow reactor, the water inlet port being configured to fluidly couple a water source to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor in the presence of the plasma; a gas outlet port coupled to the flow reactor, the gas outlet port being configured to remove the gas from the internal chamber of the flow reactor; and a water output port coupled to the flow reactor, the water output port being configured to remove the water from the internal chamber of the flow reactor. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both.

[0010] Exemplary embodiments are illustrated in referenced figures. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] **FIG. 1A – FIG. 1B** depicts in accordance with various embodiments of the present invention, electron distribution of cold nanosecond pulsed plasma (high electron energy, low temperature plasma) (FIG. 1A), and photograph of cold plasma plume 3 cm long, 2 mm in diameter (FIG. 1B).

[0012] **FIG. 2A – FIG. 2B** depicts in accordance with various embodiments of the present invention, experimental setup used to demonstrate the plasma-enhanced SO_x scrubber technology (FIG. 2A), and a schematic diagram used to demonstrate the plasma-enhanced SO_x scrubber technology (FIG. 2B).

[0013] **FIG. 3** depicts in accordance with various embodiments of the present invention a system for plasma-based SO_x and NO_x remediation.

[0014] **FIG. 4A – FIG. 4C** depicts in accordance with various embodiments of the present invention a transient plasma formed by a high voltage nanosecond pulse approach (FIG. 4A), an electron distribution of cold nanosecond pulsed plasma (FIG. 4B), and a cold plasma plume (FIG. 4C).

[0015] **FIG. 5A – FIG. 5B** depicts in accordance with various embodiments of the present invention a plot of the output voltage of a first type of pulse generator (FIG. 5A), and a plot of the output voltage of a second type of pulse generator (FIG. 5B).

[0016] **FIG. 6** depicts in accordance with various embodiments of the present invention a plot of the SO₂ removal efficiency measured as a function of the fraction of engine power needed to produce the plasma.

[0017] **FIG. 7** depicts in accordance with various embodiments of the present invention an emission spectrum from a pulsed discharge in water.

[0018] **FIG. 8A – FIG. 8C** depicts in accordance with various embodiments of the present invention, a schematic diagram of the experimental setup used to test the transient pulsed plasma reactor (FIG. 8A), typical output characteristics of nanosecond high voltage pulse generator (FIG. 8B), and photograph of the transient plasma (hot electron, low-temperature plasma) formed by the high voltage nanosecond pulse (FIG. 8C).

[0019] **FIG. 9A – FIG. 9B** depicts in accordance with various embodiments of the present invention, a temperature dependent SO₂ remediation study on approximately 600 ppmV synthetic SO₂ in a humidified air matrix (FIG. 9A), and a temperature dependent SO₂ remediation study on approximately 600 ppmV synthetic SO₂ in a humidified air matrix (FIG. 9B).

[0020] **FIG. 10A – FIG. 10B** depicts in accordance with various embodiments of the present invention, a plasma emission spectra of OH radicals observed from high voltage

discharge in aqueous solution (FIG. 10A), and a SERS-enhanced vibrational spectrum of SO₂-plasma exposed Ag nanoparticles (FIG. 10B).

[0021] FIG. 11A – FIG. 11C depicts in accordance with various embodiments of the present invention a schematic diagram of the experimental setup used to test the transient pulsed plasma reactor (FIG. 11A), typical output characteristics of nanosecond high voltage pulse generator (FIG. 11B), and a photograph of the transient plasma (hot electron, low-temperature plasma) formed by the high voltage nanosecond pulse approach (FIG. 11C).

[0022] FIG. 12A – FIG. 12B depicts in accordance with various embodiments of the present invention NO and NO_x gas concentrations with and without the plasma discharge under both dry” (i.e., without water aerosol) and “wet” (i.e., water aerosol) conditions, low plasma density (FIG. 12A), and high plasma density (FIG. 12B).

[0023] FIG. 13A - FIG. 13C depicts in accordance with various embodiments of the present invention plasma emission spectra of OH radicals (FIG. 13A), atomic oxygen observed from high voltage discharge in aqueous solution (FIG. 13B), and SERS-enhanced spectrum of NO-plasma exposed Ag nanoparticles (FIG. 13C).

[0024] FIG. 14 depicts in accordance with various embodiments of the present invention a schematic showing possible chemical pathways for NO_x remediation via plasma-based treatment.

[0025] FIG. 15 depicts in accordance with various embodiments of the present invention a schematic showing possible chemical pathways for SO_x remediation via plasma-based treatment.

[0026] FIG. 16 depicts in accordance with various embodiments of the present invention a photograph of Transient Plasma Emissions Remediation (TPER) and scrubber coupling.

[0027] FIG. 17A – FIG. 17C depicts in accordance with various embodiments of the present invention a plasma-enhanced static scrubber apparatus (FIG. 17A), without Transient Plasma Emissions Remediation (TPER) (FIG. 17B), and with Transient Plasma Emissions Remediation (TPER) (FIG. 17C).

[0028] FIG. 18 depicts in accordance with various embodiments of the present invention a photograph of a dynamic scrubber and wet reactor apparatus. The development of this system

represents apparatus for both studies, when pulser is turned off it is a dynamic scrubber and when turned on is a wet reactor.

DETAILED DESCRIPTION OF THE INVENTION

[0029] All references cited herein are incorporated by reference in their entirety as though fully set forth. Unless defined otherwise, technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0030] One skilled in the art will recognize many methods and materials similar or equivalent to those described herein, which could be used in the practice of the present invention. Other features and advantages of the invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, various features of embodiments of the invention. Indeed, the present invention is in no way limited to the methods and materials described. For convenience, certain terms employed herein, in the specification, examples and appended claims are collected here.

[0031] Unless stated otherwise, or implicit from context, the following terms and phrases include the meanings provided below. Unless explicitly stated otherwise, or apparent from context, the terms and phrases below do not exclude the meaning that the term or phrase has acquired in the art to which it pertains. Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It should be understood that this invention is not limited to the particular methodology, protocols, and reagents, etc., described herein and as such can vary. The definitions and terminology used herein are provided to aid in describing particular embodiments, and are not intended to limit the claimed invention, because the scope of the invention is limited only by the claims.

[0032] As used herein the term “comprising” or “comprises” is used in reference to compositions, methods, systems, articles of manufacture, apparatus, and respective component(s) thereof, that are useful to an embodiment, yet open to the inclusion of unspecified elements, whether useful or not. It will be understood by those within the art that, in general, terms used herein are generally intended as “open” terms (e.g., the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted

as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). Although the open-ended term “comprising,” as a synonym of terms such as including, containing, or having, is used herein to describe and claim the invention, the present invention, or embodiments thereof, may alternatively be described using alternative terms such as “consisting of” or “consisting essentially of.”

[0033] Unless stated otherwise, the terms “a” and “an” and “the” and similar references used in the context of describing a particular embodiment of the application (especially in the context of claims) can be construed to cover both the singular and the plural. The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (for example, “such as”) provided with respect to certain embodiments herein is intended merely to better illuminate the application and does not pose a limitation on the scope of the application otherwise claimed. The abbreviation, “e.g.” is derived from the Latin *exempli gratia*, and is used herein to indicate a non-limiting example. Thus, the abbreviation “e.g.” is synonymous with the term “for example.” No language in the specification should be construed as indicating any non-claimed element essential to the practice of the application.

[0034] “Optional” or “optionally” means that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not.

[0035] “SO_x” means sulfur oxides. Non-limiting examples of sulfur oxides include SO, SO₂, SO₃, SO₄, S₂O, S₂O₂, S₇O₂, S₆O₂, etc.

[0036] “NO_x” means nitrogen oxides. Non-limiting examples of nitrogen oxides include NO, NO₂, NO₃, N₂O, N₄O, N₂O₃, N₂O₄, N₂O₅, etc.

[0037] The term “non-thermal plasma” as used herein means a plasma in which the electron energies (e.g., 30 eV or $T=10^5$ K) and the vibrational modes of the molecules in the plasma (e.g., close to room temperature) are out of thermal equilibrium.

[0038] In some embodiments, the numbers expressing quantities of reagents, properties such as concentration, reaction conditions, and so forth, used to describe and claim certain embodiments of the invention are to be understood as being modified in some instances by the term “about.” Accordingly, in some embodiments, the numerical parameters set forth in the written description and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as practicable. The numerical values presented in some embodiments of the invention may contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0039] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member can be referred to and claimed individually or in any combination with other members of the group or other elements found herein. One or more members of a group can be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is herein deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[0040] Herein, we disclose a method for enhancing the performance of wet SO_x scrubber treatments (i.e., pollution control devices) by coupling a transient nanosecond pulsed plasma to the exhaust gas matrix. While existing technologies exist for reducing particulate matter (PM) and NO_x efficiently (i.e., DPFs and SCR_s), effective methods for removing SO_x are still very much lacking. SO_x wet scrubber technologies are severely limited by the low solubility of SO₂ in water, which is 10¹⁰ times lower than the solubility of H₂SO₄. Our plasma-based technology converts SO₂ to H₂SO₄ with high efficiency, thus, enabling near unity capture of sulfur products.

[0041] Our transient pulsed plasma is generated by a nanosecond high voltage pulse developed at USC. This transient pulsed approach consumes far less energy in the creation of the plasma than conventional RF sources. 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 30eV ($T=10^5\text{K}$), while the vibrational modes of the molecules remain at room temperature. These “hot” electrons enable new chemical pathways to be driven in the remediation of harmful sulfur oxide species. For example, atomic oxygen is one of the highly reactive chemical species that is produced in this cold plasma.

[0042] Using the simple experimental setup shown in FIG. 2A we have demonstrated a 7-fold improvement in SO_2 capture (from 6.6% to 44%). Here, a synthetic gas mixture containing 225PPM of SO_2 is bubbled through 100ml H_2O , while the residual gas is analyzed using a Horiba portable gas analyzer (FIG. 2B). Without the plasma, we observe a reduction in the SO_2 concentration to 210PPM due to the capture in water (FIG. 2B). This represents a 6.6% reduction in SO_2 . When the same SO_2 synthetic gas mixture is first passed through a transient plasma reactor (2” diameter) and then bubbled through 100ml H_2O , the SO_2 content of the residual gas drops to 125 PPM, which corresponds to a 44% reduction in the SO_2 (FIG. 2B). Based on these values, we are able to achieve a 7-fold improvement in SO_2 capture (from 6.6% to 44%), demonstrating the effectiveness of the transient plasma to improve or enhance the SO_x removal efficiency. The main mechanism here is that the plasma converts SO_2 to H_2SO_4 , which has a solubility that is orders of magnitude higher than SO_2 . This transient plasma-based approach enables SO_x scrubbers to be designed with improved efficiencies using small volumes of water.

[0043] Our preliminary experiments have indicated that when an exhaust gas containing sulfur dioxide is subjected to a non-thermal plasma discharge, an amount of sulfuric acid (proportional to the energy density of the discharge) is formed. This sulfuric acid, when dissolved in a given volume of water, increases its ability to retain more sulfur dioxide than without the sulfuric acid, i.e. the solubility of sulfur dioxide in acidic water is higher than in neutral water. Furthermore, numerical simulations have shown that the bottleneck chemical reaction in the conversion of sulfur dioxide to sulfuric acid is $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$. Therefore, increasing the concentration of water downstream of the discharge will increase the rate of this reaction and lead to higher remediation. These two benefits can be realized in an apparatus in which the exhaust gas is pumped from the bottom of a vertical manifold in which water is sprayed from the top and the plasma is discharged close to the water side. The acidified water captures sulfur dioxide that is flowing upward after which it gets drained at the bottom. In the presence of water, the transient plasma produces OH radicals ($\cdot\text{OH}$), which drive the rate

limiting step from $\text{SO}_2 \rightarrow \text{HSO}_3$, and the subsequent conversion to H_2SO_4 . This step is particularly important because of the strong reverse reaction from $\text{SO}_3 \rightarrow \text{SO}_2$.

[0044] Using the experimental setup shown in FIG. 16 and FIG. 17A – FIG. 17C we wanted to determine if exhaust TPER treatment prior to scrubbing mechanism enhances scrubber performance. Without being bound by theory, we hypothesized that the remediation pathway of SO_2 removal leads to the conversion of $\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$ as a final product. The solubility of H_2SO_4 is much greater than SO_2 , therefore repackaging sulfur in the form of the more soluble H_2SO_4 should result in the scrubber removing significantly more sulfur for a given quantity of scrubber water and power. Table 1, Table 2, and Table 3 below show the test parameters we used.

Table 1. Gas Component Variables

Gas Component Variables	
Zero grade air - or - $\Phi^* = 0.1$ to 1	Flow rates typically 5-10 slpm
H_2O	Flow rates: 0.2 – 0.5 mL/min

* Φ represents shorthand notation for varying ratios of N_2 , O_2 , CO_2 , and H_2O . $\Phi = 0.3$ is the proxy used for diesel exhaust composition referenced to the Detroit Diesel.

Table 2. Composition Percentages (mass fractions)

Composition Percentages (mass fractions)				
Φ	N_2 %	O_2 %	H_2O %	CO_2 %
0.1	76.18	20.83	0.86	2.14
0.2	75.67	18.39	1.70	4.24

0.3	75.16	15.98	2.54	6.32
0.4	74.66	13.61	3.36	8.37

Table 3. Scrubber Solution Variables

Scrubber Solution Variables	
Empty – no solution	Acts as H ₂ O trap for control expts
Deionized H ₂ O	Volume of scrubber solution typically 100-250 mL
Tap H ₂ O	
Acidified H ₂ O	
Salt H ₂ O (S = 35)	

[0045] Using the experimental setup shown in FIG. 16 and FIG. 17A – FIG. 17C we hypothesized that Engineering controls could enable a sufficient amount kinetic evolution time for SO₃ (formed by TPER remediation of SO₂) to convert to H₂SO₄. If this conversion occurred prior to capture by a scrubber, the scrubber solution could then effectively capture the H₂SO₄ thereby acidifying the scrubber solution. This change in the scrubber matrix allows for more non-converted SO₂ to be captured by the scrubber. Experiments were conducted where the scrubber matrix was varied including acidified water with sulfuric acid as a proxy for gaseous sulfuric acid being deposited, tap water, and a salt solution with a salinity of 35 (similar to sea water). No enhancement of scrubber efficiency was found by varying the scrubber solution content. Table 4 below shows the test parameters we used.

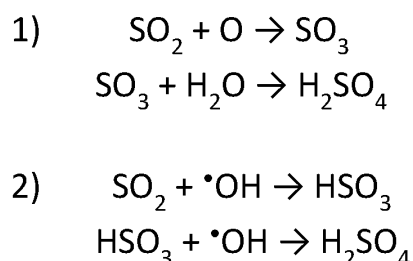
Table 4. Static Scrubber Data

Treatment	Scrub. vol., mL	Initial SO ₂ ppm	Final SO ₂ ppm	ΔSO ₂ ppm
$\Phi = 0.3$, 6.48 slpm, mass fractions: N ₂ 75.2% O ₂ 16.0% CO ₂ 6.3% H ₂ O 2.4%				
Pulser + H ₂ O inject ¹	0	485	470	15
Scrubber only, tap H ₂ O	100	480	50	430
Pulser + H ₂ O inject ¹ + Scrubber	100	480	50	430
Pulser + H ₂ O inject ¹	0	470	450	20
Air, 6.48 slpm				
Pulser + H ₂ O inject ¹	0	480	450	30
Pulser only	0	480	450	30
Pulser + H ₂ O inject ²	0	480	450	30
Pulser + H ₂ O inject ³	0	480	450	30
Pulser + H ₂ O inject ¹ doubled kinetic evolution time with longer line	0	480	450	30

H₂O inject¹ rate: 0.2 mL/minH₂O inject² rate: 0.4 mL/minH₂O inject³ rate: 1 mL/min

[0046] Our static scrubber experiments showed (1) SO₂ remediation efficiencies are the same across all parameters tested in these experiments, (2) The water reservoir acting as a static scrubber removes the same amount of SO₂ with or without TPER, and (3) The amount of SO₂ removed by the scrubber is not affected by changing the composition of the water reservoir with the parameters tested. In conclusion, (1) The TPER remediation of 500 ppm of SO₂ with energy densities of 25 J/L is 15-30 ppm. This represents a remediation of 3.6 g/kWh, and is independent of gas composition and water injection rate under the conditions shown, (2) The kinetics indicate that for full conversion from SO₃ → H₂SO₄ the residence time needed in a hot, humid environment is on the order of 3 minutes. With the scrubber positioned where it is, the kinetics are “frozen” at that time and further evolution from SO₃ to H₂SO₄ is quenched, and (3) Scrubber efficiency is independent of the content of scrubber solution under conditions tested.

[0047] Using the dynamic scrubber and wet reactor shown in FIG. 18 we designed a remediation system a remediation system in which water is injected in the vicinity of the plasma discharge. It is postulated that this discharge in the presence of liquid water can generate a higher population of hydroxyl radicals (•OH)_n. The resulting OH radicals (•OH), if sufficient in concentration, will improve the conversion of SO₂ to H₂SO₄. Without being bound by theory we hypothesized that there are two pathways to acid formation for SO₂:



[0048] Our test objectives for the dynamic scrubber and wet reactor shown in FIG. 18 were (1) Determine if injection of water (vaporized) *upstream* of the plasma may help prevent arcing; (2) Determine if injection of water (condensed) *downstream* of the plasma may help improve remediation by producing an increased concentration of OH radicals and acids; and (3) To directly quantify the impact of competition of PM with SO₂ remediation by removing the competition of NO_x with SO₂ remediation.

[0049] As shown in the dynamic scrubber and wet reactor shown in FIG. 18, (1) Water sprays downward, much like a regular scrubber; (2) Plasma is discharged in this region to create OH radicals and possibly some acids which can increase the absorbance of NO_x and SO_x; (3) The greater abundance of OH radicals may also aid in selective remediation of SO₂ over NO_x; (4) Treated water is collected and neutralized; and (5) The development of this system represents apparatus for both studies, when pulser is turned off it is a dynamic scrubber and when turned on is a wet reactor.

[0050] FIG. 3 shows a system for gas (e.g., exhaust gas) remediation that includes a flow reactor coupled to a gas source (not shown). For example, if the gas source is an engine, the gas source (e.g., engine) emits gas (e.g., exhaust gas) that includes SO_x molecules, including SO₂. In some implementations, the engine is a diesel engine, and the exhaust gas is diesel exhaust. Generally, SO₂ is produced as a by-product of the burning of fossil fuels containing sulfur compounds, such as on ships. SO₂ is considered to be an environmental criteria pollutant. The plasma reactor includes an internal chamber that is fluidly connected to the engine such that the exhaust gas flows into the internal chamber. An electrode is disposed within the internal chamber of the plasma reactor. The electrode is electrically coupled to an electrical pulse source via the electrical feedthrough. The electrical pulse source repeatedly delivers electrical pulses to the electrode to form a plasma from the exhaust gas.

[0051] In some implementations, the flow reactor forms a cylindrical stainless-steel anode, and the electrode is a center wire cathode electrode. The pulse generator can be a high voltage nanosecond pulse generator, such as a Transient Plasma Systems Model 30X or a Transient Plasma Systems Model 40X. FIG. 4A illustrates a transient plasma (e.g., a hot electron, low-temperature plasma) that can be formed by the flow reactor using the high voltage nanosecond approach. FIG. 4B shows the electron distribution of cold nanosecond pulsed plasma. FIG. 4C shows a cold plasma plume that is about 3 centimeters in diameter and about 2 millimeters in length.

[0052] The Model 40X pulse generator has a peak voltage of about 33 kilovolts (kV), a pulse rise time of about 17 nanoseconds (ns), a full width half maximum (FWHM) of about 30 ns, a maximum energy per pulse of about 88 millijoules (mJ), and a maximum repetition rate of about 800 hertz (Hz). The Model 30X has a peak voltage of about 40 kV, a pulse rise time of about 7 ns, a FWHM of about 10 ns, a maximum energy per pulse of about 66 mJ, and a maximum repetition rate of about 200 Hz. FIG. 5A is a plot of the output voltage of the Model

40X pulse generator, showing the peak voltage of about 33 kV. FIG. 5B is a plot of the output voltage of the Model 30X pulse generator, showing the peak voltage of about 40 kV. Generally, nanosecond pulsed plasma consumes less energy during the creation of the plasma as compared to radio frequency (RF)-based plasma reactors, and thus draws very little current during creation. Nanosecond pulsed plasma is thus extremely efficient from an energy and power standpoint.

[0053] Referring back to FIG. 3, the system also includes a water source that is configured to inject water into the flow reactor. In the implementation illustrated in FIG. 3, the water source is formed from a nozzle fluidly coupled to a water reservoir or other storage tank or device. The nozzle is configured to aerosolize the water such that the water is injected into the flow reactor in the form of water droplets. The water can also be in the form of water vapor.

[0054] During operation, the water is injected into the internal chamber of the flow reactor as the electrical pulses are delivered to the electrode to form the plasma. As the pulsing occurs, molecules of the hydroxyl radical (denoted by the symbol $\cdot\text{OH}$) are generated. The $\cdot\text{OH}$ molecules are the neutral form of the hydroxide ion (OH^-), which is formed as part of the self-ionization (or autoionization) of the water. One mechanism for production of the $\cdot\text{OH}$ molecules is to inject water into the internal chamber of the flow reactor. The electrical pulses delivered to the electrode free an electron from the hydroxide ions, thus forming the $\cdot\text{OH}$ molecules.

[0055] The SO_2 molecules react with $\cdot\text{OH}$ molecules to form HSO_3 molecules, which in turn react with $\cdot\text{OH}$ molecules and water molecules to form H_2SO_4 molecules. The H_2SO_4 molecules can then be removed from the flow reactor using a wet scrubber, which utilizes water molecules to remove the H_2SO_4 molecules with near unity capture. The capture of the H_2SO_4 molecules is governed by the solubility of H_2SO_4 in water, and the nature of complete acid dissociation. In some implementations, the capture rate of the H_2SO_4 molecules (e.g., the amount of water molecules needed to capture the H_2SO_4 molecules) is about 90%, between about 90% and about 100 %, about 95%, or greater than about 99%. Generally, existing wet scrubber technologies are severely limited by the low solubility of SO_2 in water, which is up to 100 times lower than the solubility of H_2SO_4 . With the system illustrated in FIG. 3, the plasma discharge in the presence of aerosol condensed phased water drives the conversion of SO_2 to H_2SO_4 , which allows for more efficient remediation of the SO_2 molecules in the exhaust gas

as compared to techniques without the use of water, which generally only achieve 35% removal efficiency.

[0056] As shown in FIG. 3, the gas (e.g., exhaust gas) generally flows through the flow reactor in a first direction. The water is injected from the nozzles in a second direction that is generally parallel and opposed to the first direction, e.g., the water droplets are injected in the opposite direction to the gas (e.g., exhaust gas) flow that is being treated. This counter-flow geometry increases the effectiveness of the water droplets both in generating the $\cdot\text{OH}$ molecules, and in removing the resulting H_2SO_4 molecules.

[0057] FIG. 6 is a plot of the SO_2 removal efficiency measured as a function of the fraction of the gas source (e.g., engine) power needed to produce the plasma, without the injection of water into the flow reactor. The SO_2 removal efficiency is measured as a percentage of the SO_2 in the gas (e.g., exhaust gas) that is removed during the remediation process. Higher efficiencies are achievable by injecting the water droplets as disclosed herein. FIG. 7 is a plot of the emission spectrum from a pulsed discharge of the flow reactor of FIG. 3 in water.

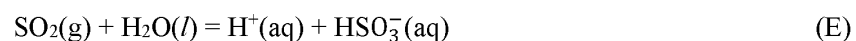
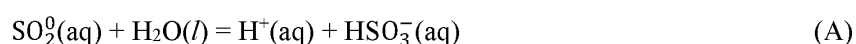
[0058] Herein we report a substantial enhancement in the removal of gaseous SO_2 by discharging a transient nanosecond pulsed plasma in a water vapor-saturated gas mixture. With the plasma alone (i.e., “dry”), the SO_2 remediation is limited to approximately 15% reduction in SO_2 (i.e., $\Delta\text{SO}_2 = 65$ ppm). In presence of water vapor, we observe 84% remediation ($\Delta\text{SO}_2 = 500$ 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: $\text{SO}_2 + \cdot\text{OH} \rightarrow \text{HSO}_3$ and the subsequent reaction of $\text{HSO}_3 + \cdot\text{OH} \rightarrow \text{H}_2\text{SO}_4$, 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).

[0059] Sulfur dioxide (SO_2) 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.

[0060] SO₂ remediation 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 $\text{NO} + \text{O} \rightarrow \text{NO}_2$. 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.

[0061] Others have 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. 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:



[0062] Once equilibrium is reached with these back reactions, the remediation is limited, and no further SO₂ 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.

[0063] In various embodiments of the present invention, 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. In various embodiments of the present invention we also provide 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.

[0064] In the work presented herein, we utilize a transient pulsed plasma discharge in a coaxial reactor. As illustrated in FIG. 8A, the plasma-based flow reactor consists of a 3 ft-long, 2 inch-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 17kV, pulse repetition rates up to 2000 Hz, and continuous powers up to 800W. Here, the plasma density is varied by adjusting the pulse repetition rate. A typical waveform produced by this pulse generator is plotted in FIG. 8B. The nanosecond pulsed plasma used here consumes far less energy in the creation of the plasma than radio frequency (RF) based 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 17kV, 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 0.5L/min after passing through a water knock out. Our synthetic gas mixture was prepared by mixing neat SO_2 gas with compressed dried air to 500 ppm by volume. Water aerosol (i.e., approximately 100nm diameter nanoparticles) was injected into the reactor using an ultrasonic nozzle. 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.

[0065] FIG. 9A shows a plot of the absolute SO₂ 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 SO₂ in air (i.e., without water vapor injection). Here, we see that only about 65 ppm (or 15%) of the SO₂ 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 SO₂ and, therefore, much of the plasma's energy goes into generating oxygen radicals which drive the back reactions to SO₂. FIG. 9A shows our results taken at moderate plasma densities (i.e., up to 100 J/L), and FIG. 9B 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 SO₂ in the humidified gas matrix.

[0066] In order to substantiate our hypothesis that OH radicals drive the intermediate steps in this SO₂ remediation reaction, we performed *in situ* plasma emission spectroscopy of our nanosecond pulsed plasma discharge with water, which shows a clear peak around 927nm, as shown in FIG. 10A. This feature is associated with charge neutral OH radicals, which correspond to highly chemically active, short lived species. These radical species produce several oxidizing agents, such as ozone and hydrogen peroxide that can be detected chemically. FIG. 10B shows surface enhanced Raman scattering (SERS)-enhanced vibrational spectra of H₂O/SO₂-plasma exposed Ag nanoparticles. Sharp peaks observed around 624 and 928cm⁻¹ are in agreement with SO₃²⁻ species, which correspond to the deprotonated HSO₃ reaction intermediate. 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 SO₂(g)/SO₂⁰(aq) equilibria and overcome the relatively low solubility of SO₂ in water, which is several orders of magnitude lower than the solubility of H₂SO₄. The H₂SO₄ can then be removed in H₂O with nearly unity capture and subsequently titrated, as is typically done in wet scrubbers.

[0067] This plasma-enhanced SO₂ remediation process may enable ships to burn high sulfur fuels while meeting the IMO SO_x 2020 emissions 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). 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.

[0068] 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: $\text{SO}_2 + \cdot\text{OH} \rightarrow \text{HSO}_3$ and $\text{HSO}_3 + \cdot\text{OH} \rightarrow \text{H}_2\text{SO}_4$. 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.

[0069] Herein we report nitrogen oxide (i.e., NO and NO₂) remediation using a transient pulsed plasma discharge in a water aerosol gas matrix using nanosecond high voltage pulses. In the conversion of NO to NO₂ using plasma-driven processes, the total removal of NO_x (i.e., NO plus NO₂) is severely limited by the back reaction of NO₂ to NO, which is also driven by the highly reactive radical species in the plasma (e.g., atomic N). By injecting water aerosol into the gas matrix, we are able to selectively drive a plasma-based reaction which minimizes the back reaction of NO₂ to NO. Here, the synergistic effect of the water aerosol and plasma discharge enables enhanced NO_x removal by creating OH radicals which, in turn, drive NO₂ to HNO₃, which is highly soluble in water. The resulting HNO₃ is then removed and titrated, as is typically done in a wet scrubber configuration. Under “dry” conditions, we only observe a 4% reduction in total NO_x due to the plasma discharge. In the presence of water aerosol, however, the plasma discharge results in a 100% reduction in NO and a 98% reduction in total NO_x. Spectroscopic evidence of the short-lived, highly reactive OH radical is obtained through plasma emission spectroscopy and the vibrational signatures of the NO₂⁻ and NO₃⁻ intermediates are observed using SERS-enhanced Raman spectroscopy. We show that the NO_x remediation increases with plasma power density demonstrating the scalability of this general approach.

[0070] In the combustion of fossil fuels, NO and NO₂ are produced as harmful pollutants giving rise to smog and acid rain. Effective NO_x (i.e., NO, NO₂) remediation remains challenging. The detailed chemical pathways associated with plasma-based remediation process are complex and not fully understood. FIG. 14 illustrates the multitude of the possible

chemical pathways in this remediation process. Here, the major products are NO_2 , N_2O , N_2O_5 , N_2 , HNO_2 , HNO_3 (indicated in boxes in FIG. 14), and the radicals assisting each reaction include various excited states of O, O_3 , OH, N, NO, and HO_2 (shown next to the corresponding arrow in FIG. 14). The reaction of NO with oxygen radicals are believed to be the dominant reactions for plasma-based remediation. The back reaction of N with NO_2 and the reaction of O_3 with NO_2 both replenish NO. Transient plasmas produced by high voltage nanosecond pulses consume far less energy in the creation of the plasma than conventional RF sources. 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. The NO removal efficiency of nanosecond pulse discharges can be as high as 0.75 mol/kWh, which is considerably higher than that obtained with (microsecond) pulsed corona discharges (0.35 mol/kWh) and dielectric barrier discharge (DBD) reactors (0.2 mol/kWh).

[0071] NO is significantly less soluble in water than both SO_2 and CO_2 . However, we have shown that plasma treatment can convert NO to NO_2 extremely efficiently. In the work presented here, we demonstrate a synergistic effect of injecting water aerosol with plasma discharge to push this reaction to HNO_3 via the creation of OH radicals. Here, we perform a comparative study of plasma discharge with (i.e., “wet”) and without (i.e., “dry”) injection of water aerosol, systematically at different plasma densities. Plasma emission spectra and Raman scattering spectra are taken in order to verify the OH and NO_3^- intermediates.

[0072] In the work presented herein, a transient plasma is created using a nanosecond pulse discharge in a coaxial reactor consisting of a 3 ft-long, 2 inch-diameter stainless steel cylindrical anode with a single-wire cathode center electrode, as depicted in FIG. 11A. A Transient Plasma Systems Model 20X pulse generator is operated with a peak output voltage of 17kV (FIG. 11B) at pulse repetition rates up to 2 kHz and continuous powers up to 0.8 kW. FIG. 11B shows a plot of a typical pulse waveform generated using this system. The recent availability of solid-state nanosecond high voltage pulse generators, which consume less energy than conventional RF plasmas, opens up the possibility of driving these NO_x remediation processes more efficiently. At a peak voltage 17kV, this system delivers a transient power of

4.76 MW. FIG. 11A illustrates the reactor configuration in which a water aerosol (i.e., approximately 100nm diameter nanoparticles) is injected into the reactor using an ultrasonic nozzle in the direction counter to the flow of NO_x to be treated. At the output of this reactor, NO and NO_x concentrations are measured using a portable gas analyzer (Horiba Model PGA-350), which samples at a flow rate of 0.5L/min. In the experiments reported here, our synthetic gas mixture was prepared by mixing neat NO gas with compressed dried air at 500 PPM by volume.

[0073] FIG. 12A shows a plot of the NO and NO_x concentrations taken with (“wet”) and without (“dry”) water aerosol injection. FIG. 12A and FIG. 12B show the results obtained at plasma densities of 18 J/L and 45 J/L, respectively. Here, we observe relatively little plasma-induced remediation in the dry gas mixtures: 40% for ΔNO and only 4% for ΔNO_x. However, a dramatic increase in NO and NO_x remediation is observed the presence of water aerosol injection: 100% for ΔNO and 98% for ΔNO_x. This marked improvement in remediation efficacy demonstrates the synergistic effects of adding water together with plasma discharge, which increases the availability of OH radicals far beyond that attained with the plasma alone or the water aerosol alone. This plasma-enhanced remediation mechanism is comprised of a two-step process, in which the NO is converted to NO₂ by atomic oxygen radicals in the plasma followed by the rapid conversion of NO₂ to HNO₃ via the OH radicals created by discharging the plasma in the presence of water aerosol. This second step minimizes the back reaction of NO₂ to NO, greatly improving the efficacy of this approach. The resulting HNO₃ is highly soluble in the water aerosol matrix is captured with near unity efficiencies and subsequently titrated.

[0074] In order to corroborate the hypothesis that OH radicals drive the NO₂ → HNO₃ step in this NO_x remediation process, *in situ* plasma emission spectroscopy was performed using nanosecond pulsed plasma discharge with water, as shown in FIG. 13A. Here, a sharp peak is observed at a wavelength around 927nm, which corresponds to charge neutral OH radicals that are short lived, highly chemically active species. These OH radical species are known to produce various oxidizing agents, such as hydrogen peroxide and ozone. Here, however, we believe the OH radicals are used directly to drive NO₂ to HNO₃, as described above. FIG. 13B shows a plasma emission spectrum centered around 777nm, which corresponds to light originating from atomic oxygen species, responsible for the first step in this remediation process (i.e., NO → NO₂). FIG. 13C shows surface enhanced Raman scattering (SERS)-

enhanced vibrational spectra of H₂O/NO₂ plasma exposed Ag nanoparticles. Sharp peaks observed around 822 and 1053 cm⁻¹ are in agreement with previous reports of NO₂⁻ and NO₃⁻ species, which correspond to the deprotonated HNO₃ reaction intermediate. These spectroscopic signatures provide further evidence of the OH-driven reaction pathway proposed for this water aerosol-enhanced, plasma-driven process. This approach circumvents the standard NO(g)/HNO₃⁰(aq) equilibria and overcomes the relatively low solubility of NO in water, which is several orders of magnitude lower than the solubility of HNO₃. The HNO₃ is then removed in H₂O with nearly unity capture and subsequently titrated, as is typical done in a wet scrubber configuration.

[0075] In conclusion, we demonstrate a synergistic effect in the remediation of toxic nitrogen oxide pollutants (i.e., NO and NO₂) by discharging a nanosecond pulsed transient plasma discharge together with injection of a water aerosol into the gas matrix. Previous studies have shown high efficiency conversion of NO to NO₂ via plasma-based processes but poor removal of total NO_x (i.e., NO and NO₂) due to the rapid back reaction of NO₂ back to NO. By comparing the plasma-based remediation with and without injection of water aerosol, we are able to isolate a reaction pathway that minimizes the back reaction of NO₂ to NO by increasing the availability of OH radicals. This results in a two-step process, whereby NO is first converted to NO₂ by atomic oxygen radicals, and then NO₂ is subsequently converted to HNO₃ via OH radicals. Here, the key reactants OH and O are evidenced by plasma emission spectroscopy, while the vibrational signatures of the HNO₃⁻ intermediate species are observed using SERS spectroscopy. Using this synergistic approach, we observe a 98% reduction in NO and a 100% reduction in total NO_x due to the plasma discharge in the presence of water aerosol. Without the plasma discharge, the NO_x removal efficiency is generally limited by the low solubility of NO and NO₂ in water. Here, we provide a way around this limitation by rapidly driving NO₂ to HNO₃, before it can be converted by the back reaction to NO.

[0076] In various embodiments, the present invention provides a system for plasma-based remediation, comprising: a flow reactor, wherein the flow reactor comprises an internal chamber and an electrode at least partially disposed within the internal chamber, the internal chamber being configured to be fluidly coupled to a gas source such that a gas from the gas source flows into the internal chamber of the flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof; a pulse generator electrically coupled to the electrode of the flow reactor, the pulse generator being configured

to deliver electrical pulses to the electrode to thereby form a plasma from the gas, the first chemical compound being converted to a second chemical compound in the plasma; and a water source fluidly coupled to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor to form $\cdot\text{OH}$ (hydroxyl radical) molecules from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, the $\cdot\text{OH}$ molecules reacting with the second chemical compound in the plasma so as to convert the second chemical compound into a water soluble chemical compound, and at least a second portion of the injected water removing the water soluble chemical compound from the flow reactor, thereby reducing the concentration of the first chemical compound in the gas. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, NO_x is NO . In some embodiments, the second chemical compound is NO_2 . In some embodiments, the water soluble chemical compound is HNO_3 . In some embodiments, SO_x is SO_2 . In some embodiments, the second chemical compound is HSO_3 . In some embodiments, the water soluble chemical compound is H_2SO_4 . In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both. In some embodiments, the first chemical compound is converted to a second chemical compound in the plasma by the $\cdot\text{OH}$ molecules reacting with the first chemical compound in the plasma so as to convert the first chemical compound to the second chemical compound.

[0077] In various embodiments, the present invention provides a system for plasma-based remediation, comprising: a flow reactor, wherein the flow reactor comprises an internal chamber and an electrode at least partially disposed within the internal chamber, the internal chamber being configured to be fluidly coupled to a gas source such that a gas from the gas source flows into the internal chamber of the flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected

from the group consisting of NO_x, SO_x, and combinations thereof; a pulse generator electrically coupled to the electrode of the flow reactor, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas; and a water source fluidly coupled to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor to form [•]OH (hydroxyl radical) molecules from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, the [•]OH molecules reacting with the first chemical compound in the plasma so as to convert the first chemical compound into a water soluble chemical compound, and at least a second portion of the injected water removing the water soluble chemical compound from the flow reactor, thereby reducing the concentration of the first chemical compound in the gas. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, NO_x is NO. In some embodiments, the water soluble chemical compound is HNO₃. In some embodiments, SO_x is SO₂. In some embodiments, the water soluble chemical compound is H₂SO₄. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both.

[0078] In various embodiments, the present invention provides a method for plasma-based remediation, comprising: receiving a gas from a gas source into an internal chamber of a flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof; delivering electric pulses to an electrode positioned in the internal chamber such that a plasma is formed from the gas, wherein the first chemical compound is converted to a second chemical compound in the plasma; injecting water into the internal chamber of the flow reactor in the presence of the plasma, wherein [•]OH (hydroxyl radical) molecules are formed from at least a first portion of the injected water when the electrical pulses are delivered to the

electrode, and wherein the $\cdot\text{OH}$ molecules react with the second chemical compound so as to convert the second chemical compound into a water soluble chemical compound; and removing at least a second portion of the injected water from the flow reactor, wherein the second portion of the injected water comprises the water soluble compound, thereby reducing the concentration of the first chemical compound in the gas. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, NO_x is NO . In some embodiments, the second chemical compound is NO_2 . In some embodiments, the water soluble chemical compound is HNO_3 . In some embodiments, SO_x is SO_2 . In some embodiments, the second chemical compound is HSO_3 . In some embodiments, the water soluble chemical compound is H_2SO_4 . In some embodiments, the electric pulses are delivered by a pulse generator. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both. In some embodiments, the first chemical compound is converted to a second chemical compound in the plasma by the $\cdot\text{OH}$ molecules reacting with the first chemical compound in the plasma so as to convert the first chemical compound to the second chemical compound.

[0079] In various embodiments, the present invention provides a method for plasma-based remediation, comprising: receiving a gas from a gas source into an internal chamber of a flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x , SO_x , and combinations thereof; delivering electric pulses to an electrode positioned in the internal chamber such that a plasma is formed from the gas; injecting water into the internal chamber of the flow reactor in the presence of the plasma, wherein $\cdot\text{OH}$ (hydroxyl radical) molecules are formed from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, and wherein the $\cdot\text{OH}$ molecules react with the first chemical compound so as to

convert the first chemical compound into a water soluble chemical compound; and removing at least a second portion of the injected water from the flow reactor, wherein the second portion of the injected water comprises the water soluble compound, thereby reducing the concentration of the first chemical compound in the gas. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments, the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, NO_x is NO. In some embodiments, the water soluble chemical compound is HNO₃. In some embodiments, SO_x is SO₂. In some embodiments, the water soluble chemical compound is H₂SO₄. In some embodiments, the electric pulses are delivered by a pulse generator. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both.

[0080] In various embodiments, the present invention provides a plasma reactor for plasma-based remediation, comprising: a flow reactor comprising an internal chamber; a gas input port coupled to the flow reactor, the gas input port being configured to fluidly couple a gas source to the flow reactor such that a gas can flow into the internal chamber of the flow reactor; an electrode at least partially disposed within the internal chamber of the flow reactor; a pulse generator electrically coupled to the electrode, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas; a water inlet port coupled to the flow reactor, the water inlet port being configured to fluidly couple a water source to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor in the presence of the plasma; a gas outlet port coupled to the flow reactor, the gas outlet port being configured to remove the gas from the internal chamber of the flow reactor; and a water output port coupled to the flow reactor, the water output port being configured to remove the water from the internal chamber of the flow reactor. In some embodiments, the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode. In some embodiments,

the extruded electrode includes a central portion and at least one arm extending from the central portion. In some embodiments, the plasma is a non-thermal plasma. In some embodiments, the pulse generator is a solid-state nanosecond high voltage pulse generator. In some embodiments, the gas is an exhaust gas. In some embodiments, the gas source is an engine. In some embodiments, the engine is a combustion engine. In some embodiments, the engine is a diesel engine. In some embodiments, the electrical pulses are high voltage nanosecond electrical pulses. In some embodiments, the electrical pulses have a repetition rate of up to 2000 Hz. In some embodiments, the water is water aerosol. In some embodiments, the water is water vapor. In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both.

[0081] In various embodiments, the second portion of the injected water removes the H_2SO_4 molecules with near unity capture. In various embodiments, the water source includes a nozzle configured to aerosolize the water such that the water is injected into the plasma in the internal chamber of the flow reactor as water droplets. In various embodiments, the exhaust gas is configured to flow through the flow reactor in a first direction, and wherein the water source is configured to inject the water into the flow reactor in a second direction. In various embodiments, the second direction is parallel and opposed to the first direction. In various embodiments, at least a first portion of the $\cdot\text{OH}$ molecule reacts with the SO_2 molecules to form HSO_3 molecules, and wherein at least a second portion of the $\cdot\text{OH}$ molecules reacts with the HSO_3 molecules to form H_2SO_4 molecules. In various embodiments, the electrode is a center wire cathode electrode. In various embodiments, the pulse generator has a peak voltage of between about 33 kilovolts and about 40 kilovolts, a pulse rise time of between about 7 nanoseconds and about 17 nanoseconds, a full width half maximum (FWHM) of between about 10 nanoseconds and about 30 nanoseconds, a maximum energy per pulse of between about 66 millijoules and about 88 millijoules, and a maximum repetition rate of between about 299 Hz and about 800 Hz. In various embodiments, the pulse generator is a high voltage nanosecond pulse generator. In various embodiments, the engine is a diesel engine.

[0082] In various embodiments, the second portion of the injected water removes the H_2SO_4 molecules with near unity capture. In various embodiments, aerosolizing the water such that the water is injected into the plasma in the internal chamber of the flow reactor as water droplets. In various embodiments, the exhaust gas flows through the flow reactor in a first direction, and wherein the water is injected into the flow reactor in a second direction. In various embodiments, the second direction is parallel and opposed to the first direction. In various embodiments, at least a first portion of the $\cdot\text{OH}$ molecules reacts with the SO_2

molecules to form HSO_3 molecules, and wherein at least a second portion of the OH molecules reacts with the HSO_3 molecules to form H_2SO_4 molecules. In various embodiments, the electrode is a center wire cathode electrode. In various embodiments, the pulse generator has a peak voltage of between about 33 kilovolts and about 40 kilovolts, a pulse rise time of between about 7 nanoseconds and about 17 nanoseconds, a full width half maximum (FWHM) of between about 10 nanoseconds and about 30 nanoseconds, a maximum energy per pulse of between about 66 millijoules and about 88 millijoules, and a maximum repetition rate of between about 299 Hz and about 800 Hz. In various embodiments, the pulse generator is a high voltage nanosecond pulse generator. In various embodiments, the engine is a diesel engine. In some embodiments, the engine is a marine diesel engine.

[0083] In various embodiments, the electrode is selected from a group comprising an extruded electrode, a 3-wire electrode, and a 4-wire electrode. In various embodiments, the extruded electrode has a cross-section that is selected from a group comprising about 2.0 inches, about 2.25 inches, or about 2.5 inches. In various embodiments, the extrude electrode has a cross-section of between about 1.0 inches and about 5.0 inches. In various embodiments, the electrode is a 3-wire electrode with a cross-section of about 2 inches. In various embodiments, the extruded electrode includes a central portion and one or more arms extending from the central portion.

[0084] In various embodiments, the present invention provides a method for reducing the concentration of SO_x in a gas stream, comprising: contacting a gas stream with electrical pulses in the presence of water to form a plasma and acidified water, wherein the gas stream comprises a concentration of SO_x ; and passing the gas stream through the acidified water to reduce the concentration of SO_x in the gas stream. In some embodiments, the SO_x is SO_2 .

[0085] In various embodiments, the present invention provides a method for reducing the concentration of SO_2 in a gas stream, comprising: contacting a gas stream with electrical pulses in the presence of water to form a plasma and acidified water, wherein the gas stream comprises a concentration of SO_2 ; and passing the gas stream through the acidified water to reduce the concentration of SO_2 in the gas stream. In some embodiments, the acidified water comprises H_2SO_4 .

[0086] In various embodiments, the present invention provides a method for reducing the concentration of NO_x in a gas stream, comprising: contacting a gas stream with electrical pulses in the presence of water to form a plasma and acidified water, wherein the gas stream

comprises a concentration of NO_x; and passing the gas stream through the acidified water to reduce the concentration of NO_x in the gas stream. In some embodiments, the NO_x is NO.

[0087] In various embodiments, the present invention provides a method for reducing the concentration of NO in a gas stream, comprising: contacting a gas stream with electrical pulses in the presence of water to form a plasma and acidified water, wherein the gas stream comprises a concentration of NO; and passing the gas stream through the acidified water to reduce the concentration of NO in the gas stream. In some embodiments, the acidified water comprises HNO₃.

[0088] In some embodiments, the plasma is a non-thermal plasma. In some embodiments, the non-thermal plasma is a transient non-thermal plasma. In some embodiments, the electrical pulses are generated by a nanosecond high voltage pulse generator. In some embodiments, the gas stream is an exhaust gas stream. In some embodiments, the exhaust gas stream is from combustion of a fuel. In some embodiments, the fuel is selected from natural gas, gasoline, petrol, biodiesel blends, diesel fuel, fuel oil, and coal. In some embodiments, the exhaust gas is from combustion of a fuel.

[0089] In some embodiments, HSO₃ is HSO₃⁻. In some embodiments, OH radical is [•]OH.

[0090] In various embodiments, the present invention provides a system for SO_x and/or NO_x remediation, comprising: a flow reactor comprising an internal chamber; a gas input port coupled to the flow reactor, the gas input port being configured to fluidly couple a gas source to the flow reactor such that a gas can flow into the internal chamber of the flow reactor; an electrode at least partially disposed within the internal chamber of the flow reactor; a pulse generator electrically coupled to the electrode; a water inlet port coupled to the flow reactor, the water inlet port being configured to fluidly couple a water source to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor; a gas outlet port coupled to the flow reactor, the gas outlet port being configured to remove the gas from the internal chamber of the flow reactor; and a water output port coupled to the flow reactor, the water output port being configured to remove the water from the internal chamber of the flow reactor.

[0091] In some embodiments, the pulse generator is configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas (e.g., the input gas). In some embodiments, the pulse generator is not powered on, and as such no plasma is formed from the

gas (e.g., the input gas). In some embodiments, the water is injected into the internal chamber of the flow reactor in the presence of the plasma. In some embodiments, the water is injected into the internal chamber of the flow reactor in the absence of the plasma. In some embodiments, the system is a dynamic scrubber. In some embodiments, the system is a wet reactor. In some embodiments, the gas comprises a concentration of NO_x, and/or a concentration of SO_x. In some embodiments, the gas being removed from the internal chamber of the flow reactor by way of the gas outlet port has a reduced concentration of SO_x and/or a reduced concentration of NO_x compared to the concentration of SO_x and/or concentration of NO_x entering into or flowing into the internal chamber of the flow reactor by way of the gas input port. In some embodiments, the water being removed from the internal chamber of the flow reactor comprises HNO₃, H₂SO₄, or both. In some embodiments, the water being removed from the internal chamber of the flow reactor is acidified water. In some embodiments, when the pulse generator is not powered on, and as such no plasma is formed from the input gas, the system is a dynamic scrubber. In some embodiments, when the pulse generator is powered on, and as such a plasma is formed from the input gas the system is a wet reactor. In some embodiments, the water added to the internal chamber of the flow reactor is input water or inlet water. In some embodiments, the water removed from the internal chamber of the flow reactor is output water or outlet water. In some embodiments, the gas added to the internal chamber of the flow reactor is input gas or inlet gas. In some embodiments, the gas removed from the internal chamber of the flow reactor is output gas or outlet gas.

[0092] In some embodiments, the flow reactor is a plasma reactor. In some embodiments, the flow reactor is a transient pulsed plasma reactor. In some embodiments, the flow reactor is a transient plasma reactor. In some embodiments, the flow reactor is a plasma-based flow reactor.

[0093] In some embodiments, the plasma reactor is a flow reactor. In some embodiments, the plasma reactor is a transient pulsed plasma reactor. In some embodiments, the plasma reactor is a transient plasma reactor.

[0094] In some embodiments, at least a portion of the flow reactor can be heated, cooled, or both. In some embodiments, at least a portion of the plasma reactor can be heated, cooled, or both. In some embodiments, at least a portion of the system for plasma-based remediation can be heated, cooled, or both.

[0095] Some embodiments of the present invention can be defined as any of the following numbered paragraphs:

1. A system for plasma-based remediation, comprising: a flow reactor, wherein the flow reactor comprises an internal chamber and an electrode at least partially disposed within the internal chamber, the internal chamber being configured to be fluidly coupled to a gas source such that a gas from the gas source flows into the internal chamber of the flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof; a pulse generator electrically coupled to the electrode of the flow reactor, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas, the first chemical compound being converted to a second chemical compound in the plasma; and a water source fluidly coupled to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor to form [•]OH (hydroxyl radical) molecules from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, the [•]OH molecules reacting with the second chemical compound in the plasma so as to convert the second chemical compound into a water soluble chemical compound, and at least a second portion of the injected water removing the water soluble chemical compound from the flow reactor, thereby reducing the concentration of the first chemical compound in the gas.
2. The system of paragraph 1, wherein the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode.
3. The system of paragraph 2, wherein the extruded electrode includes a central portion and at least one arm extending from the central portion.
4. The system of paragraph 1, wherein the plasma is a non-thermal plasma.
5. The system of paragraph 1, wherein NO_x is NO.
6. The system of paragraph 5, wherein the second chemical compound is NO₂.
7. The system of paragraph 6, wherein the water soluble chemical compound is HNO₃.
8. The system of paragraph 1, wherein SO_x is SO₂.
9. The system of paragraph 8, wherein the second chemical compound is HSO₃.
10. The system of paragraph 9, wherein the water soluble chemical compound is H₂SO₄.
11. The system of paragraph 1, wherein the pulse generator is a solid-state nanosecond high voltage pulse generator.
12. The system of paragraph 1, wherein the gas is an exhaust gas.

13. The system of paragraph 1, wherein the gas source is an engine.
14. The system of paragraph 13, wherein the engine is a combustion engine.
15. The system of paragraph 13, wherein the engine is a diesel engine.
16. The system of paragraph 1, wherein the electrical pulses are high voltage nanosecond electrical pulses.
17. The system of paragraph 1, wherein the electrical pulses have a repetition rate of up to 2000 Hz.
18. The system of paragraph 1, wherein the water is water aerosol.
19. The system of paragraph 1, wherein the water is water vapor.
20. The system of paragraph 1, wherein at least a portion of the flow reactor can be heated, cooled, or both.
21. A method for plasma-based remediation, comprising: receiving a gas from a gas source into an internal chamber of a flow reactor, wherein the gas comprises a concentration of a first chemical compound, wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof; delivering electric pulses to an electrode positioned in the internal chamber such that a plasma is formed from the gas, wherein the first chemical compound is converted to a second chemical compound in the plasma; injecting water into the internal chamber of the flow reactor in the presence of the plasma, wherein 'OH (hydroxyl radical) molecules are formed from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, and wherein the 'OH molecules react with the second chemical compound so as to convert the second chemical compound into a water soluble chemical compound; and removing at least a second portion of the injected water from the flow reactor, wherein the second portion of the injected water comprises the water soluble compound, thereby reducing the concentration of the first chemical compound in the gas.
22. The method of paragraph 21, wherein the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode.
23. The method of paragraph 22, wherein the extruded electrode includes a central portion and at least one arm extending from the central portion.
24. The method of paragraph 21, wherein the plasma is a non-thermal plasma.
25. The method of paragraph 21, wherein NO_x is NO.
26. The method of paragraph 25, wherein the second chemical compound is NO₂.
27. The method of paragraph 26, wherein the water soluble chemical compound is HNO₃.
28. The method of paragraph 21, wherein SO_x is SO₂.

29. The method of paragraph 28, wherein the second chemical compound is HSO_3 .
30. The method of paragraph 29, wherein the water soluble chemical compound is H_2SO_4 .
31. The method of paragraph 21, wherein the electric pulses are delivered by a pulse generator.
32. The method of paragraph 31, wherein the pulse generator is a solid-state nanosecond high voltage pulse generator.
33. The method of paragraph 21, wherein the gas is an exhaust gas.
34. The method of paragraph 21, wherein the gas source is an engine.
35. The method of paragraph 34, wherein the engine is a combustion engine.
36. The method of paragraph 34, wherein the engine is a diesel engine.
37. The method of paragraph 21, wherein the electrical pulses are high voltage nanosecond electrical pulses.
38. The method of paragraph 21, wherein the electrical pulses have a repetition rate of up to 2000 Hz.
39. The method of paragraph 21, wherein the water is water aerosol.
40. The method of paragraph 21, wherein the water is water vapor.
41. The method of paragraph 21, wherein at least a portion of the flow reactor can be heated, cooled, or both.
42. A plasma reactor for plasma-based remediation, comprising: a flow reactor comprising an internal chamber; a gas input port coupled to the flow reactor, the gas input port being configured to fluidly couple a gas source to the flow reactor such that a gas can flow into the internal chamber of the flow reactor; an electrode at least partially disposed within the internal chamber of the flow reactor; a pulse generator electrically coupled to the electrode, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas; a water inlet port coupled to the flow reactor, the water inlet port being configured to fluidly couple a water source to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor in the presence of the plasma; a gas outlet port coupled to the flow reactor, the gas outlet port being configured to remove the gas from the internal chamber of the flow reactor; and a water output port coupled to the flow reactor, the water output port being configured to remove the water from the internal chamber of the flow reactor.
43. The plasma reactor of paragraph 42, wherein the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode.

44. The plasma reactor of paragraph 43, wherein the extruded electrode includes a central portion and at least one arm extending from the central portion.
45. The plasma reactor of paragraph 42, wherein the plasma is a non-thermal plasma.
46. The plasma reactor of paragraph 42, wherein the pulse generator is a solid-state nanosecond high voltage pulse generator.
47. The plasma reactor of paragraph 42, wherein the gas is an exhaust gas.
48. The plasma reactor of paragraph 42, wherein the gas source is an engine.
49. The plasma reactor of paragraph 48, wherein the engine is a combustion engine.
50. The plasma reactor of paragraph 48, wherein the engine is a diesel engine.
51. The plasma reactor of paragraph 42, wherein the electrical pulses are high voltage nanosecond electrical pulses.
52. The plasma reactor of paragraph 42, wherein the electrical pulses have a repetition rate of up to 2000 Hz.
53. The plasma reactor of paragraph 42, wherein the water is water aerosol.
54. The plasma reactor of paragraph 42, wherein the water is water vapor.
55. The plasma reactor of paragraph 42, wherein at least a portion of the flow reactor can be heated, cooled, or both.

[0096] To provide aspects of the present disclosure, embodiments may employ any number of programmable processing devices that execute software or stored instructions. Physical processors and/or machines employed by embodiments of the present disclosure for any processing or evaluation may include one or more networked (Internet, cloud, WAN, LAN, satellite, wired or wireless (RF, cellular, WiFi, Bluetooth, etc.)) or non-networked general purpose computer systems, microprocessors, field programmable gate arrays (FPGAs), digital signal processors (DSPs), micro-controllers, smart devices (e.g., smart phones), computer tablets, handheld computers, and the like, programmed according to the teachings of the exemplary embodiments. In addition, the devices and subsystems of the exemplary embodiments can be implemented by the preparation of application-specific integrated circuits (ASICs) or by interconnecting an appropriate network of conventional component circuits. Thus, the exemplary embodiments are not limited to any specific combination of hardware circuitry and/or software.

[0097] Stored on any one or on a combination of computer readable media, the exemplary embodiments of the present disclosure may include software for controlling the devices and subsystems of the exemplary embodiments, for driving the devices and subsystems of the

exemplary embodiments, for enabling the devices and subsystems of the exemplary embodiments to interact with a human user, and the like. Such software can include, but is not limited to, device drivers, firmware, operating systems, development tools, applications software, database management software, and the like. Computer code devices of the exemplary embodiments can include any suitable interpretable or executable code mechanism, including but not limited to scripts, interpretable programs, dynamic link libraries (DLLs), Java classes and applets, complete executable programs, and the like. Moreover, processing capabilities may be distributed across multiple processors for better performance, reliability, cost, or other benefits.

[0098] Common forms of computer-readable media may include, for example, a floppy disk, a flexible disk, a hard disk, magnetic tape, any other suitable magnetic medium, a CD-ROM, CDRW, DVD, any other suitable optical medium, punch cards, paper tape, optical mark sheets, any other suitable physical medium with patterns of holes or other optically recognizable indicia, a RAM, a PROM, an EPROM, a FLASH-EPROM, any other suitable memory chip or cartridge, a carrier wave or any other suitable medium from which a computer can read. Such storage media can also be employed to store other types of data, e.g., data organized in a database, for access, processing, and communication by the processing devices.

[0099] The various methods and techniques described above provide a number of ways to carry out the application. Of course, it is to be understood that not necessarily all objectives or advantages described can be achieved in accordance with any particular embodiment described herein. Thus, for example, those skilled in the art will recognize that the methods can be performed in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objectives or advantages as taught or suggested herein. A variety of alternatives are mentioned herein. It is to be understood that some preferred embodiments specifically include one, another, or several features, while others specifically exclude one, another, or several features, while still others mitigate a particular feature by inclusion of one, another, or several advantageous features.

[00100] Furthermore, the skilled artisan will recognize the applicability of various features from different embodiments. Similarly, the various elements, features and steps discussed above, as well as other known equivalents for each such element, feature or step, can be employed in various combinations by one of ordinary skill in this art to perform methods in accordance with the principles described herein. Among the various elements, features, and

steps some will be specifically included and others specifically excluded in diverse embodiments.

[00101] Although the application has been disclosed in the context of certain embodiments and examples, it will be understood by those skilled in the art that the embodiments of the application extend beyond the specifically disclosed embodiments to other alternative embodiments and/or uses and modifications and equivalents thereof.

EXAMPLES

[00102] The invention is further illustrated by the following examples which are intended to be purely exemplary of the invention, and which should not be construed as limiting the invention in any way. The following examples are illustrative only, and are not intended to limit, in any manner, any of the aspects described herein. The following examples are provided to better illustrate the claimed invention and are not to be interpreted as limiting the scope of the invention. To the extent that specific materials are mentioned, it is merely for purposes of illustration and is not intended to limit the invention. One skilled in the art may develop equivalent means or reactants without the exercise of inventive capacity and without departing from the scope of the invention.

[00103] Example 1.

[00104] Preliminary Results: Using the simple experimental setup shown in FIG. 2A, we have demonstrated a 7-fold improvement in SO₂ capture (from 6.6% to 44%). Here, a synthetic gas mixture containing 225PPM of SO₂ is bubbled through 100ml H₂O, while the residual gas is analyzed using a Horiba portable gas analyzer (FIG. 2B). Without the plasma, we observe a reduction in the SO₂ concentration to 210PPM due to the capture in water (FIG. 2B). This represents a 6.6% reduction in SO₂. When the same SO₂ synthetic gas mixture is first passed through a transient plasma reactor (2" diameter) and then bubbled through 100ml H₂O, the SO₂ content of the residual gas drops to 125 PPM, which corresponds to a 44% reduction in the SO₂ (FIG. 2B). Based on these values, we are able to achieve a 7-fold improvement in SO₂ capture (from 6.6% to 44%), demonstrating the effectiveness of the transient plasma to improve or enhance the SO_x removal efficiency. The main mechanism here is that the plasma converts SO₂ to H₂SO₄, which has a solubility that is orders of magnitude higher than SO₂. This transient plasma-based approach enables SO_x scrubbers to be designed with improved efficiencies using small volumes of water.

[00105] Our preliminary experiments have indicated that when an exhaust gas containing sulfur dioxide is subjected to a non-thermal plasma discharge, an amount of sulfuric acid (proportional to the energy density of the discharge) is formed. This sulfuric acid, when dissolved in a given volume of water, increases its ability to retain more sulfur dioxide than without the sulfuric acid, i.e. the solubility of sulfur dioxide in acidic water is higher than in neutral water. Furthermore, numerical simulations have shown that the bottleneck chemical reaction in the conversion of sulfur dioxide to sulfuric acid is $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$. Therefore, increasing the concentration of water downstream of the discharge will increase the rate of this reaction and lead to higher remediation. These two benefits can be realized in an apparatus in which the exhaust gas is pumped from the bottom of a vertical manifold in which water is sprayed from the top and the plasma is discharged close to the water side. The acidified water captures sulfur dioxide that is flowing upward after which it gets drained at the bottom. In the presence of water, the transient plasma produces $\cdot\text{OH}$ radicals, which drive the rate limiting step from $\text{SO}_2 \rightarrow \text{HSO}_3$, and the subsequent conversion to H_2SO_4 . This step is particularly important because of the strong reverse reaction from $\text{SO}_3 \rightarrow \text{SO}_2$.

[00106] Preferred embodiments of this application are described herein, including the best mode known to the inventors for carrying out the application. Variations on those preferred embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. It is contemplated that skilled artisans can employ such variations as appropriate, and the application can be practiced otherwise than specifically described herein. Accordingly, many embodiments of this application include all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the application unless otherwise indicated herein or otherwise clearly contradicted by context.

[00107] All patents, patent applications, publications of patent applications, and other material, such as articles, books, specifications, publications, documents, things, and/or the like, referenced herein are hereby incorporated herein by this reference in their entirety for all purposes, excepting any prosecution file history associated with same, any of same that is inconsistent with or in conflict with the present document, or any of same that may have a limiting affect as to the broadest scope of the claims now or later associated with the present document. By way of example, should there be any inconsistency or conflict between the description, definition, and/or the use of a term associated with any of the incorporated material

and that associated with the present document, the description, definition, and/or the use of the term in the present document shall prevail.

[00108] It is to be understood that the embodiments of the application disclosed herein are illustrative of the principles of the embodiments of the application. Other modifications that can be employed can be within the scope of the application. Thus, by way of example, but not of limitation, alternative configurations of the embodiments of the application can be utilized in accordance with the teachings herein. Accordingly, embodiments of the present application are not limited to that precisely as shown and described.

[00109] Various embodiments of the invention are described above in the Detailed Description. While these descriptions directly describe the above embodiments, it is understood that those skilled in the art may conceive modifications and/or variations to the specific embodiments shown and described herein. Any such modifications or variations that fall within the purview of this description are intended to be included therein as well. Unless specifically noted, it is the intention of the inventors that the words and phrases in the specification and claims be given the ordinary and accustomed meanings to those of ordinary skill in the applicable art(s).

[00110] The foregoing description of various embodiments of the invention known to the applicant at this time of filing the application has been presented and is intended for the purposes of illustration and description. The present description is not intended to be exhaustive nor limit the invention to the precise form disclosed and many modifications and variations are possible in the light of the above teachings. The embodiments described serve to explain the principles of the invention and its practical application and to enable others skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed for carrying out the invention.

[00111] While particular embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that, based upon the teachings herein, changes and modifications may be made without departing from this invention and its broader aspects and, therefore, the appended claims are to encompass within their scope all such changes and modifications as are within the true spirit and scope of this invention.

CLAIMS

What is claimed is:

1. A system for plasma-based remediation, comprising:

a flow reactor,

wherein the flow reactor comprises an internal chamber and an electrode at least partially disposed within the internal chamber, the internal chamber being configured to be fluidly coupled to a gas source such that a gas from the gas source flows into the internal chamber of the flow reactor,

wherein the gas comprises a concentration of a first chemical compound,

wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof;

a pulse generator electrically coupled to the electrode of the flow reactor, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas, the first chemical compound being converted to a second chemical compound in the plasma; and

a water source fluidly coupled to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor to form [•]OH (hydroxyl radical) molecules from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, the [•]OH molecules reacting with the second chemical compound in the plasma so as to convert the second chemical compound into a water soluble chemical compound, and at least a second portion of the injected water removing the water soluble chemical compound from the flow reactor, thereby reducing the concentration of the first chemical compound in the gas.

2. The system of claim 1, wherein the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode.

3. The system of claim 2, wherein the extruded electrode includes a central portion and at least one arm extending from the central portion.

4. The system of claim 1, wherein the plasma is a non-thermal plasma.

5. The system of claim 1, wherein NO_x is NO.
6. The system of claim 5, wherein the second chemical compound is NO₂.
7. The system of claim 6, wherein the water soluble chemical compound is HNO₃.
8. The system of claim 1, wherein SO_x is SO₂.
9. The system of claim 8, wherein the second chemical compound is HSO₃.
10. The system of claim 9, wherein the water soluble chemical compound is H₂SO₄.
11. The system of claim 1, wherein the pulse generator is a solid-state nanosecond high voltage pulse generator.
12. The system of claim 1, wherein the gas is an exhaust gas.
13. The system of claim 1, wherein the gas source is an engine.
14. The system of claim 13, wherein the engine is a combustion engine.
15. The system of claim 13, wherein the engine is a diesel engine.
16. The system of claim 1, wherein the electrical pulses are high voltage nanosecond electrical pulses.
17. The system of claim 1, wherein the electrical pulses have a repetition rate of up to 2000 Hz.
18. The system of claim 1, wherein the water is water aerosol.
19. The system of claim 1, wherein the water is water vapor.
20. The system of claim 1, wherein at least a portion of the flow reactor can be heated, cooled, or both.
21. A method for plasma-based remediation, comprising:
 - receiving a gas from a gas source into an internal chamber of a flow reactor,
 - wherein the gas comprises a concentration of a first chemical compound,

wherein the first chemical compound is selected from the group consisting of NO_x, SO_x, and combinations thereof;

delivering electric pulses to an electrode positioned in the internal chamber such that a plasma is formed from the gas,

wherein the first chemical compound is converted to a second chemical compound in the plasma;

injecting water into the internal chamber of the flow reactor in the presence of the plasma,

wherein [•]OH (hydroxyl radical) molecules are formed from at least a first portion of the injected water when the electrical pulses are delivered to the electrode, and

wherein the [•]OH molecules react with the second chemical compound so as to convert the second chemical compound into a water soluble chemical compound; and

removing at least a second portion of the injected water from the flow reactor,

wherein the second portion of the injected water comprises the water soluble compound, thereby reducing the concentration of the first chemical compound in the gas.

22. The method of claim 21, wherein the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode.

23. The method of claim 22, wherein the extruded electrode includes a central portion and at least one arm extending from the central portion.

24. The method of claim 21, wherein the plasma is a non-thermal plasma.

25. The method of claim 21, wherein NO_x is NO.

26. The method of claim 25, wherein the second chemical compound is NO₂.

27. The method of claim 26, wherein the water soluble chemical compound is HNO₃.

28. The method of claim 21, wherein SO_x is SO₂.

29. The method of claim 28, wherein the second chemical compound is HSO_3 .
30. The method of claim 29, wherein the water soluble chemical compound is H_2SO_4 .
31. The method of claim 21, wherein the electric pulses are delivered by a pulse generator.
32. The method of claim 31, wherein the pulse generator is a solid-state nanosecond high voltage pulse generator.
33. The method of claim 21, wherein the gas is an exhaust gas.
34. The method of claim 21, wherein the gas source is an engine.
35. The method of claim 34, wherein the engine is a combustion engine.
36. The method of claim 34, wherein the engine is a diesel engine.
37. The method of claim 21, wherein the electrical pulses are high voltage nanosecond electrical pulses.
38. The method of claim 21, wherein the electrical pulses have a repetition rate of up to 2000 Hz.
39. The method of claim 21, wherein the water is water aerosol.
40. The method of claim 21, wherein the water is water vapor.
41. The method of claim 21, wherein at least a portion of the flow reactor can be heated, cooled, or both.
42. A plasma reactor for plasma-based remediation, comprising:
- a flow reactor comprising an internal chamber;
 - a gas input port coupled to the flow reactor, the gas input port being configured to fluidly couple a gas source to the flow reactor such that a gas can flow into the internal chamber of the flow reactor;
 - an electrode at least partially disposed within the internal chamber of the flow reactor;

a pulse generator electrically coupled to the electrode, the pulse generator being configured to deliver electrical pulses to the electrode to thereby form a plasma from the gas;

a water inlet port coupled to the flow reactor, the water inlet port being configured to fluidly couple a water source to the internal chamber of the flow reactor, the water source being configured to inject water into the internal chamber of the flow reactor in the presence of the plasma;

a gas outlet port coupled to the flow reactor, the gas outlet port being configured to remove the gas from the internal chamber of the flow reactor; and

a water output port coupled to the flow reactor, the water output port being configured to remove the water from the internal chamber of the flow reactor.

43. The plasma reactor of claim 42, wherein the electrode is selected from the group consisting of a three-wire electrode, a four-wire electrode, and an extruded electrode.

44. The plasma reactor of claim 43, wherein the extruded electrode includes a central portion and at least one arm extending from the central portion.

45. The plasma reactor of claim 42, wherein the plasma is a non-thermal plasma.

46. The plasma reactor of claim 42, wherein the pulse generator is a solid-state nanosecond high voltage pulse generator.

47. The plasma reactor of claim 42, wherein the gas is an exhaust gas.

48. The plasma reactor of claim 42, wherein the gas source is an engine.

49. The plasma reactor of claim 48, wherein the engine is a combustion engine.

50. The plasma reactor of claim 48, wherein the engine is a diesel engine.

51. The plasma reactor of claim 42, wherein the electrical pulses are high voltage nanosecond electrical pulses.

52. The plasma reactor of claim 42, wherein the electrical pulses have a repetition rate of up to 2000 Hz.

- 53. The plasma reactor of claim 42, wherein the water is water aerosol.
- 54. The plasma reactor of claim 42, wherein the water is water vapor.
- 55. The plasma reactor of claim 42, wherein at least a portion of the flow reactor can be heated, cooled, or both.