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FLUE GAS PURIFICATION METHODTECHNICAL FIELD

The present invention relates to a flue gas purification method, and more particularly, the present invention relates to a flue gas purification method incorporating dry injection and wet scrubbing unit operations to substantially eliminate SO_x and NO_x compounds as well as other air toxic compounds from the flue gas.

BACKGROUND ART

10 In view of new stringent legislation in the United States and elsewhere, greater strides have now had to be made concerning fossil fuels. As is well known, the use of fossil fuels significantly contributes to air pollution and a multitude of patents have issued with the objective of
15 mitigating the pollution aspect.

Globally, the prior art establishes a number of wet chemical absorption methods which primarily incorporate wet scrubbers where a hot contaminated gas is scrubbed or detoxified in a gas liquid contact apparatus with a
20 neutralizing solution. The neutralizing solution can typically be any suitable aqueous alkaline liquid or slurry to remove sulfur oxides and other contaminants present in the flue gas stream. The gas liquid contacts apparatus are generally employed by power generating stations and use the
25 wet chemical absorption arrangement incorporating sodium, calcium, magnesium, etc. to desulfurize flue gas.

Johnson et al., in United States Patent No. 6,303,083; issued October 16, 2001, disclose a SO_x removal process for

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flue gas treatment. A specific particle size range for the sorbent is reacted with the flue gas to reduce SO_3 content. The treated flue gas is then reacted in a wet scrubber to reduce SO_2 content.

5 Further processes which have been incorporated in industry to remove sulfur trioxide include condensation reactions. An example of such a process is referred to as the WSA-SNOX process. This method involves the catalytic conversion of sulfur dioxide to sulfur trioxide. The
10 sulfur trioxide is then removed by condensation in the form of sulfur acid.

As is evident from the existing flue gas management protocols, NO and NO_x formation present complications in terms of plume control. Consequently, the existence of the
15 plume requires additional unit operations and still results in the existence of the plume at tolerable levels.

The wet scrubbing systems that employ lime, limestone, soda ash or other alkaline compositions demonstrate efficacy for removal of sulfur dioxide, but are
20 significantly less efficient at the removal of sulfur trioxide or sulfuric acid aerosol.

In light of the increasing stringent pollution regulations, there clearly exists a need for the management of flue gas where both the SO_x and NO_x compounds can be
25 handled effectively without emission of brown plume, the need to augment with suppressants or the combination of equipment which, in the case of the wet flue gas desulfurization and wet electrostatic precipitation, only

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marginally addresses the problem at a fairly significant expense.

The methodology set forth herein alleviates all of the limitations in the prior art techniques.

5 **DISCLOSURE OF THE INVENTION**

One object of the present invention is to provide an improved method for flue gas purification.

A further object of one embodiment of the present invention is to provide a method of scrubbing SO_x and NO_x
10 compounds from a flue gas stream, comprising:

a dry injection scrubbing operation and a wet scrubbing operation, the dry injection scrubbing operation including:

15 contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent for removing substantially all of the SO_x and a large amount of NO_x compounds present in the stream; and

the wet scrubbing operation including:

20 contacting the stream to remove any residual SO_x and NO_x compounds remaining in the stream.

The unification of the dry injection scrubbing operation and a wet scrubbing operation advantageously eliminates the concern for brown plume. Previously, reaction of the sodium sorbents resulted in the synthesis
25 of NO_x compounds as plume. The NO_x compounds are soluble species and are easily managed by treatment with the wet scrubbing operation. In this manner, it is immaterial that

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NO₂ forms; the plume cannot develop since the NO_x (where x=>1 and Y=>2) species are absorbed in the wet scrubber. Accordingly, the previous requirement for auxiliary suppressant addition is obviated.

5 In the combined system set forth herein, the flue gas is preconditioned by absorbent injection. The absorbent can comprise suitable reagents or sorbents known to at least diminish the concentration of the sulfur trioxide. Advantageously, this can be achieved by wet or dry
10 injection with essentially any sorbent or combinations of sorbent and at any possible location in the system. Dry sodium bicarbonate injection has been found to be particularly effective since it reacts with the sulfur di- and trioxides as well as the NO_x compounds. Generally
15 speaking, the sulfur trioxide is managed to a level that is compatible with single stage wet electrostatic precipitators installed in a wet flue gas desulfurization tower.

A further object of one embodiment of the presentation
20 is to provide a method of scrubbing SO_x and NO_x compounds from a flue gas stream, comprising:

a dry injection scrubbing operation and a wet scrubbing operation, the dry injection scrubbing operation including:

25 contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent for removing substantially all of the SO_x and a large amount of NO_x compounds present in the stream;

the wet scrubbing operation including:

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contacting the stream to remove any residual SO_x and NO_x compounds remaining in the stream; and recirculating unreacted sorbent to the wet scrubbing operation.

5 A still further object of one embodiment of the present invention is to provide a method of scrubbing SO_x and NO_x compounds from a flue gas stream, comprising:

a dry injection scrubbing operation and a wet scrubbing operation, the dry injection scrubbing
10 operation including:

contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent for removing substantially all of the SO_x and a large amount of NO_x compounds present in the stream; and

15 the wet scrubbing operation including:

scrubbing the stream from the dry injection scrubbing operation in the presence of an oxidant to remove any residual SO_x and NO_x compounds remaining in the stream.

20 As a particular benefit, the processes set forth herein are useful to capture air toxics including, as examples, mercury, particulates and a host of heavy metals.

As set forth herein previously, prior art attempts relating to the conversion of NO₂ were problematic since a
25 brown plume of NO₂ was not captured by downstream equipment. By the combination of the technology set forth herein, the wet scrubbing operation efficiently captures the NO₂, N₂O₃ and N₂O₅ and other N_xO_y compounds. In

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addition, at least a portion of the NO is captured by the sodium bicarbonate.

Yet another object of one embodiment of the present invention is to provide a method of scrubbing SO_x and NO_x compounds from a flue gas stream, comprising:

a wet injection scrubbing operation and a wet scrubbing operation, the wet injection scrubbing operation including:

contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent solution for removing substantially all of the SO_x and a large amount of NO_x compounds present in the stream; and

the wet scrubbing operation including:

contacting the stream to remove any residual SO_x and NO_x compounds remaining in the stream.

The provision of the oxidant augments the effectiveness of the wet scrubbing and in particular, the oxidation of the NO_x compounds.

20 **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a schematic illustration of a vertical combustor facility used to generate test data; and

Figure 2 is a schematic illustration of the process according to one embodiment.

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It will be noted that throughout the appended drawings, like features are identified by like reference numerals.

BEST MODE FOR CARRYING OUT THE INVENTION

5

EXPERIMENTAL

The apparatus employed to gather the data is illustrated in Figure 1. The vertical combustor, globally denoted by numeral 10, was the primary combustor for generating the data.

10

Bituminous coal from silo 12 was pulverized in pulverizer 14 and passed on to silo 16 and subsequently into coal feeder 18. Pre-dried and pulverized coal was conveyed to the combustor via an eductor 20.

15

The combustor 10 produced NO_x emissions of about 400 - 500 ppm_{dv} at 2% O₂ excess at the combustor exit and SO_x emissions at 2700 to 3000 ppm.

Flue gas compositions (O₂, CO₂, CO, NO and NO₂) were monitored using flue gas analyzer 22 located between the combustor 10 and cyclone 24.

20

For emission control, the combustor 10 was equipped with a hot cyclone, a five-field electrostatic precipitator (ESP) 30 and the condensing heat exchanger 28 (used as a wet scrubber).

25

Dry NaHCO₃ powder was injected against the flue stream in a counter current manner in ports 20a, 20b, and 20c.

Table 1 sets forward the conditions under which the data was obtained.

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Table 1 - Conditions Common to All Tests			
Coal		Bituminous	
Heat input		0.21 MWth (0.7 MBTU/hr)	
Target O ₂ excess in flue gas		2% volume dry	
Target NO _x concentration		400 ppm _{dv}	
Flue gas velocity at 150 °C		~ 3.4 m/s (11 ft/sec)	
Scrubbing solution flow rate		~ 34 l/min (9 USGPM)	
NaHCO ₃ injection duration		1 hour,	
NaHCO ₃ in-flight residence time		0.5, 1.5 and 3 sec	
NaHCO ₃ injection temperature		150°C	
Conditions Specific to Each Test			
Test ID	NaHCO ₃ Injection Rate	NaHCO ₃ Size	Scrubbing Solution
_0	6.6 kg/hr	45 µm	Na ₂ CO ₃
_1	6.6 kg/hr	20 µm	Pre-charged
_2	5.5 kg/hr	20 µm	Pre-charged
_3	7.7 kg/hr	20 µm	Pre-charged
Injection Port			
Port ID	Residence time from Port to inlet (sec)		
20a	3		
20b	1.5		
20c	0.5		

Test _0 was a base test to ensure that all components were operational. In this test, the NaHCO₃ was first injected in each port for 5 min. Then, a 1-hour long injection was done in Port 20a.

The scrubber pre-charging was done according to the following specifications: 1 kg of Na₂CO₃, 29 kg of Na₂SO₄ and 19 kg of Na₂SO₃ dissolved in 187 l of water. The pH of the prepared solution was about 10.6.

Table 2 represents the analysis of the coal used.

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Table 2 - Coal analysis	
Proximate Analysis (wt %)	
Moisture	1.14
Ash	11.03
Volatiles	39.3
Fixed Carbon	48.53
Ultimate Analysis (wt %, dry)	
Carbon	72.42
Hydrogen	4.99
Nitrogen	1.37
Sulphur	3.96
Ash	11.03
Oxygen (diff)	6.10
Chlorine (Cl)	790 ppm
Fluorine (F)	72 ppm
Mercury (Hg)	0.086 ppm

All combustion trials were conducted at a firing rate of 0.21 MWt (0.7 MBTU/hr) with the O₂ in flue gas being maintained at 2 % dv.

- 5 Prior to commencing each suite of combustion trials with a specific coal, natural gas was burned at 0.3 MWt for at least 8h with 5 vol% O₂ in the flue gas to perform instrumentation checks and to attain thermal equilibrium in the combustor 10 and downstream heat exchanger 28.

10 EXAMPLE 1

NaHCO₃ was injected at 150°C for a short period (5 minutes) in all three ports 20a, 20b, 20c at a rate of 6.6 kg/hr to observe its effects on the concentrations of SO₂ and NO_x. A 1-hour continuous injection was then performed
15 in Port 20a following the short injections.

Sodium carbonate (Na₂CO₃) in water solution was used in scrubber 28 as the scrubbing solution and was added

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during the testing period to maintain the solution pH at around 7.

Table 3 summarizes the average flue gas compositions at the combustor exit and scrubber inlet before any NaHCO_3 injection was made.

Table 3 - Flue gas compositions before injections		
	Combustor Exit	Scrubber inlet
O_2 (%)	2.08 ± 0.32	5.41 ± 0.22
CO_2 (%)	16.21 ± 0.38	13.65 ± 0.26
CO (ppm)	50 ± 154	100 ± 142
NO_x (ppm)	493 ± 54	226 ± 24
SO_2 (ppm)	2854 ± 114	2331 ± 58

Note that all concentrations are reported on a volumetric and dry basis.

10 Injection of sodium bicarbonate started at 0240 pm at Port 20c (0.5 sec residence time), then proceeded to Ports 20b and 20a lasting for 5 min at each port. Table 4 summarizes the flue gas compositions during the injection period.

Table 4 - Flue gas compositions at combustor exit and scrubber inlet during the short period (5 min) sorbent injections						
	Port 20c		Port 20b		Port 20a	
	Comb. Exit	Scrubber inlet	Comb. Exit	Scrubber inlet	Comb. Exit	Scrubber inlet
O_2 (%)	2.6 ± 0.4	7.2 ± 0.5	2.3 ± 0.3	7.1 ± 0.3	2.3 ± 0.2	6.9 ± 0.1
CO_2 (%)	15.6 ± 0.4	11.9 ± 0.3	16.3 ± 0.3	12.0 ± 0.2	16.1 ± 0.0	12.4 ± 0.0
CO (ppm)	35 ± 30	67 ± 78	15 ± 26	28 ± 24	8 ± 3	19 ± 9

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NO _x (ppm)	491 ± 13	204 ± 11	488 ± 13	193 ± 13	512 ± 10	162 ± 7
SO ₂ (ppm)	2687 ± 96	1637 ± 117	2853 ± 30	1570 ± 97	2919 ± 57	1344 ± 44

Table 5 shows the flue gas compositions during the 1-hour injection in Port 20a:

Table 5 - Flue gas compositions at combustor exit, scrubber inlet and outlet during the 1-hour sorbent injections in Port 20a			
	Comb. Exit	Scrubber Inlet	Scrubber Outlet
O ₂ (%)	2.3 ± 0.2	6.9 ± 0.1	7.0 ± 0.3
CO ₂ (%)	16.1 ± 0.3	12.3 ± 0.2	12.4 ± 0.2
CO (ppm)	30 ± 107	36 ± 80	10 ± 1
NO _x (ppm)	515 ± 19	152 ± 11	170 ± 7
SO ₂ (ppm)	2862 ± 42	1115 ± 45	15 ± 2

5 A significant reduction in concentration of the SO₂ and NO_x was realized immediately upon injection of the NaHCO₃ into the flue gas stream. The effect was enhanced with increasing residence time. Once the NaHCO₃ injection was complete, the concentrations of SO₂ and NO_x returned to
10 pre-injection levels.

A further test was done with NaHCO₃ injection in three ports at a flow rate of 6.6 kg/hr and target injection temperature of 150°C. The injection period lasted 1 hour in each port.

15 The NaHCO₃ injection started in Port 20c and proceeded to Ports 20b and 20a.

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Table 6 summarizes the average flue gas compositions at the combustor exit and scrubber inlet before any NaHCO_3 injection was made.

Table 6 - Flue gas compositions before injections		
	Combustor Exit	Scrubber inlet
O_2 (%)	1.87 ± 0.44	4.48 ± 0.49
CO_2 (%)	16.42 ± 0.42	14.11 ± 0.41
CO (ppm)	27 ± 109	46 ± 56
NO_x (ppm)	492 ± 47	408 ± 36
SO_2 (ppm)	2969 ± 68	2591 ± 157

- 5 Injection of NaHCO_3 started at 1254 am at Port 20c (0.5 sec residence time), proceeded to Ports 20b and 20a and lasted for 60 min in each port. Table 7 summarizes the flue gas compositions during the injections.

Table 7 - Flue gas compositions during injections			
Port 20c			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O_2 (%)	6.10 ± 0.47	5.68 ± 0.18	5.66 ± 0.12
CO_2 (%)	13.35 ± 0.44	13.41 ± 0.28	13.37 ± 0.09
CO (ppm)	45 ± 47	97 ± 142	36 ± 44
NO (ppm)	356 ± 18	215 ± 13	252 ± 13
NO_2 (ppm)	6 ± 2	27 ± 4	4 ± 2
NO_x (ppm)	362 ± 21	242 ± 12	256 ± 15
SO_2 (ppm)	2385 ± 64	296 ± 30	11 ± 2

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Port 20b			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	5.71 ± 0.45	5.67 ± 0.14	5.68 ± 0.17
CO ₂ (%)	13.46 ± 0.48	13.67 ± 0.00	13.50 ± 0.00
CO (ppm)	43 ± 45	43 ± 71	23 ± 23
NO (ppm)	317 ± 24	182 ± 13	202 ± 13
NO ₂ (ppm)	8 ± 2	41 ± 3	6 ± 4
NO _x (ppm)	325 ± 24	223 ± 12	208 ± 13
SO ₂ (ppm)	2167 ± 204	245 ± 34	18 ± 4
Port 20a			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	5.96 ± 0.05	5.74 ± 0.12	5.80 ± 0.19
CO ₂ (%)	13.07 ± 0.00	13.54 ± 0.27	13.41 ± 0.00
CO (ppm)	13 ± 0	21 ± 32	14 ± 11
NO (ppm)	344 ± 21	113 ± 11	118 ± 12
NO ₂ (ppm)	14 ± 3	76 ± 5	11 ± 5
NO _x (ppm)	358 ± 21	189 ± 12	128 ± 14
SO ₂ (ppm)	2282 ± 38	160 ± 16	11 ± 3

As is evident , a noticeable decrease of NO and SO₂ upon the injection of NaHCO₃ and the increase of NO₂ was realized. The scrubber was very effective at removing SO₂ as its concentration dropped precipitously at the scrubber outlet.

EXAMPLE 2

This test was done with NaHCO₃ injection in three ports at a flow rate of 5.5 kg/hr and injection temperature of 150°C. The injection period was 1 hour in each port. The scrubber solution was pre-charged with: 1 kg of Na₂CO₃, 29 kg of Na₂SO₄ and 19 kg of Na₂SO₃ dissolved in 187

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l of water. The pH of the prepared solution was about 10.6.

The NaHCO_3 injection started in Port 20c and proceeded to Ports 20b and 20a. After the completion of each injection, the filter of the CEM train downstream of the injection port was immediately changed to ensure accurate readings of the flue gas compositions.

Table 8 summarizes the average flue gas compositions at the combustor exit and scrubber inlet before any NaHCO_3 injection was made.

Table 8 - Flue gas compositions before injections		
	Combustor Exit	Scrubber inlet
O_2 (%)	2.07 ± 0.30	4.28 ± 0.34
CO_2 (%)	16.17 ± 0.30	14.52 ± 0.33
CO (ppm)	10 ± 46	21 ± 24
NO_x (ppm)	515 ± 57	321 ± 27
SO_2 (ppm)	2937 ± 86	2438 ± 77

Injection of NaHCO_3 started at 1237am at Port 20c (0.5 sec residence time), proceeded to Port 20a lasting for 60 min at each port. Table 9 summarizes the flue gas compositions during the injections.

Table 9 - Flue gas compositions during injections			
Port 20c			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O_2 (%)	6.18 ± 0.63	6.05 ± 0.14	6.21 ± 0.16
CO_2 (%)	13.84 ± 0.44	13.48 ± 0.26	13.41 ± 0.10
CO (ppm)	87 ± 151	17 ± 11	12 ± 12
NO (ppm)	277 ± 33	203 ± 22	211 ± 23
NO_2 (ppm)	0 ± 0	5 ± 3	7 ± 4
NO_x (ppm)	277 ± 33	208 ± 21	218 ± 24

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SO ₂ (ppm)	2208 ± 70	159 ± 21	11 ± 2
Port 20b			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	6.18 ± 0.24	6.26 ± 0.13	6.49 ± 0.14
CO ₂ (%)	12.94 ± 0.28	13.23 ± 0.09	13.23 ± 0.22
CO (ppm)	30 ± 65	10 ± 9	6 ± 1
NO (ppm)	280 ± 15	150 ± 23	181 ± 21
NO ₂ (ppm)	4 ± 2	45 ± 4	1 ± 2
NO _x (ppm)	284 ± 16	195 ± 26	183 ± 22
SO ₂ (ppm)	2364 ± 68	Decreasing to 150	90 ± 9
Port 20a			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	6.37 ± 0.17	6.36 ± 0.11	6.35 ± 0.16
CO ₂ (%)	12.88 ± 0.23	12.96 ± 0.20	13.45 ± 0.00
CO (ppm)	13 ± 18	10 ± 11	12 ± 18
NO (ppm)	320 ± 35	113 ± 9	125 ± 12
NO ₂ (ppm)	10 ± 3	58 ± 3	2 ± 3
NO _x (ppm)	330 ± 36	171 ± 12	128 ± 12
SO ₂ (ppm)	2303 ± 39	326 ± 24	18 ± 3

From a review of the data noted above, there was a noticeable decrease of NO and SO₂ upon the injection of NaHCO₃ and a significant increase of NO₂ at scrubber inlet at 2 and 3 sec residence time. When the CEM was moved to scrubber outlet at the end of the third injection, it indicated the immediate increase of the concentrations of NO₂ and SO₂ confirming their removal in the scrubber.

EXAMPLE 3

In the example, NaHCO₃ injection occurred in three ports at a flow rate of 7.7kg/hr and injection temperature of 150°C. The injection period lasted 1 hour in each port.

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The scrubber solution was pre-charged as 1 kg of Na_2CO_3 , 29 kg of Na_2SO_4 and 19 kg of Na_2SO_3 dissolved in 187 l of water. The pH of the prepared solution was about 10.6.

The NaHCO_3 injection started in Port 20c and proceeded
5 to Port 20a.

Table 10 shows the average injection temperatures for each port.

Table 10 - Average injection temperatures (°C)						
	Port 20a		Port 20b		Port 20c	
	Upstream	Downstream	Upstream	Downstream	Upstream	Downstream
Injection temperature	155±3	132±5	157±1	133±0	157±5	139±5

Table 11 summarizes the average flue gas compositions
10 at the combustor exit and scrubber inlet before any NaHCO_3 injection was made.

Table 11 - Flue gas compositions before injections		
	Combustor Exit	Scrubber inlet
O_2 (%)	2.14 ± 0.33	4.38 ± 0.19
CO_2 (%)	15.95 ± 0.29	14.23 ± 0.45
CO (ppm)	10 ± 85	28 ± 5
NO_x (ppm)	545 ± 114	540 ± 25
SO_2 (ppm)	2964 ± 127	2672 ± 101

Injection of sodium bicarbonate started at 1237am at
Port C (0.5 sec residence time), proceeded to Port A
15 lasting for 60 min at each port.

Table 12 summarizes the flue gas compositions during the injections.

Table 12 - Flue gas compositions during injections

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Port 20c			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	5.82 ± 0.38	6.05 ± 0.10	6.11 ± 0.16
CO ₂ (%)	12.89 ± 0.38	13.25 ± 0.00	13.02 ± 0.17
CO (ppm)	20 ± 1	17 ± 1	14 ± 1
NO (ppm)	480 ± 54	303 ± 28	341 ± 19
NO ₂ (ppm)	7 ± 5	38 ± 4	6 ± 2
NO _x (ppm)	486 ± 61	342 ± 34	346 ± 20
SO ₂ (ppm)	2464 ± 57	Decreasing to 130	12
Port 20b			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	5.98 ± 0.22	5.85 ± 0.11	5.79 ± 0.10
CO ₂ (%)	13.05 ± 0.22	13.45 ± 0.16	13.22 ± 0.00
CO (ppm)	15 ± 2	17 ± 36	15 ± 15
NO (ppm)	457 ± 7	275 ± 20	286 ± 19
NO ₂ (ppm)	22 ± 3	58 ± 7	4 ± 1
NO _x (ppm)	479 ± 7	333 ± 23	290 ± 19
SO ₂ (ppm)	2303 ± 58	300 - 400	10 ± 1
Port 20a			
	Scrubber inlet before injection (diluted by injection air)	Scrubber inlet during injection	Scrubber outlet during injection
O ₂ (%)	5.67 ± 0.32	5.86 ± 0.08	5.74 ± 0.12
CO ₂ (%)	13.23 ± 0.27	13.36 ± 0.03	13.31 ± 0.15
CO (ppm)	25 ± 25	11 ± 3	13 ± 8
NO (ppm)	510 ± 12	224 ± 13	202 ± 8
NO ₂ (ppm)	26 ± 6	88 ± 3	3 ± 2
NO _x (ppm)	536 ± 11	312 ± 14	206 ± 7
SO ₂ (ppm)	2303 ± 39	218 ± 16	8 ± 1

There was a decrease of NO and SO₂ upon the injection of NaHCO₃ and a pronounced increase of NO₂ at the scrubber inlet at all 3 residence times tested. Accordingly, at this injection rate (7.7 kg/hr), the accumulation of NaHCO₃

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powder on the CEM filter was quite rapid. During the third injection at Port 20a, the CEM was first located at the scrubber outlet and moved to the scrubber inlet at the end of the injection in order to obtain a more reliable SO₂ reading.

The last 3 tests all showed that, upon injection of NaHCO₃ in the flue stream, concentrations of SO₂ and NO decreased immediately, while NO₂ concentration increased. Once the injection was stopped, the concentrations of SO₂ and NO rapidly returned to the pre-injection levels. The NaHCO₃ injection did not have any effect on the concentrations of the other monitored species (O₂, CO₂ and CO).

For all three tests, the scrubber solution was pre-charged according to 1 kg of Na₂CO₃, 29 kg of Na₂SO₄ and 19 kg of Na₂SO₃ dissolved in 187 l of water. The pH of the prepared solution was about 10.6. When the scrubbing started, the pH value decreased slowly as sulfur was dissolved in the solution. However, when the NaHCO₃ injection started, the pH value of the scrubbing solution stayed steady at about 7.5.

From Table 13, it can be seen that the scrubber was very effective in removing NO₂ produced in the flue stream after the injection of NaHCO₃. The scrubber was also very effective at removing SO₂.

Having described the test facility and the data collected, in connection with establishing the effectiveness of the injection and scrubbing operations, reference will now be made to Figure 2 which schematically

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illustrates one embodiment of a plant design. The overall plant design is referenced by numeral 40 with the combustion system from, for example, a power station being referenced by numeral 42. The combustion products are
5 first treated in an electrostatic precipitator or baghouse 44 and subsequently discharged through a flue gas duct 46. In an attempt to further increase the efficiency of the overall system, oxidant material may be injected into the flue gas duct at any number of locations such as at or
10 approximate the inlet 48 or approximate the outlet 50. At this oxidation step, is useful to convert uncaptured NO and NO₂ to be converted to NO₂, N₂O₃, N₂O₅ and N_xO_y *inter alia*. The oxidation steps 48 and 50 are augmented by the injection step with sodium bicarbonate, the injection being
15 broadly denoted by numeral 52. Although the sodium bicarbonate injection step is preferentially a dry injection step, it will be clearly understood by those skilled in the art that the injection step can also be wet with essentially any alkali compound and at any of several
20 locations from the flue gas duct to the wet scrubber to be discussed hereinafter.

Suitable oxidants will be appreciated by those skilled, however, examples include hydrogen peroxide, ozone, sodium chlorate or compounds (NaClO_x where x is 1
25 through 4) or any combination of these materials. Once having been treated with a dry injection step, the flue gas stream now partially devoid of NO_x compounds is treated in a wet to dry transition device 54 and then subsequently on to the wet scrubbing operation in wet scrubber 56. Any
30 suitable scrubber 56 may be incorporated and will be essentially the choice of the designer based on the

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requirements of the overall circuit. Typical manufactures of wet scrubbers include The Babcock and Wilcox Company, Marsulex, Kawaski Heavy Industries, Mitsui, Chiyoda, Thyssen KEA, *inter alia*. Numerals 58 and 60 denote further
5 possible oxidant injection points where the aqueous solution of the oxidant is recirculated into the scrubber 56. A suitable pump 62 may be included with each circulation loop of the oxidant. These steps are optional, since it has been indicated herein previously that the
10 oxidant can be introduced at any point from the flue gas duct to the wet scrubber and still function to achieve the goal of oxidizing any compounds present. The solution from scrubber 56, broadly denoted by numeral 64 may be removed from time to time for processing.

15 As a further optional step, a wet electrostatic precipitator may be introduced into the circuit, the former being represented by numeral 66 where the gas stream is passed through the electrostatic precipitator to polish the flue gas of any further particulate, fine particulates,
20 water droplets or aerosols from the stream. This is an optional step and is not essential to the process. Once through the ESP 66, the flue gas can then be discharged through the stack 68. The wet esp 66 may or may not be an extension to the wet scrubber 56. An alternative, shown in
25 dashed lines is illustrated in Figure 2.

In terms of the overall reactions that occur in the process, the reactions that occur in the dry injection phase are simply those that involve the sodium bicarbonate contacting the SO_x and NO_x compounds. Exemplary of the

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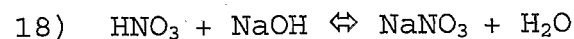
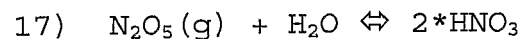
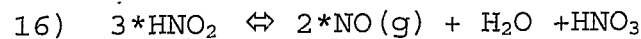
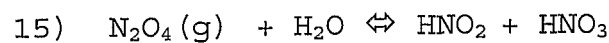
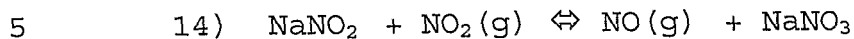
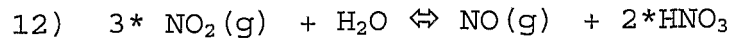
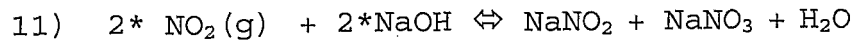
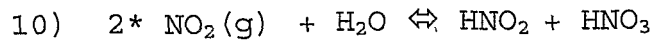
actions of the SO_x chemistry that occur in the injection apparatus include the following:

- 1) $\text{NaHCO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- 2) $2*\text{NaHCO}_3 + \text{SO}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_3 + 2*\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- 5 3) $2*\text{NaHCO}_3 + \text{SO}_3(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_4 + 2*\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- 4) $\text{Na}_2\text{CO}_3 + \text{SO}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_3 + \text{CO}_2(\text{g})$
- 5) $\text{Na}_2\text{CO}_3 + \text{SO}_3(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{CO}_2(\text{g})$
- 6) $2*\text{NaNO}_3 + \text{SO}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_4 + 2*\text{NO}_2(\text{g})$
- 7) $2*\text{NaNO}_2 + \text{SO}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_4 + 2*\text{NO}(\text{g})$
- 10 8) $2*\text{NaNO}_2 + \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{SO}_4 + 2*\text{NO}_2(\text{g})$
- 9) $\text{SO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3 + \text{H}$

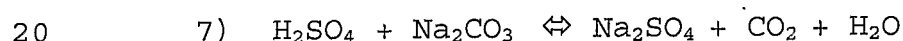
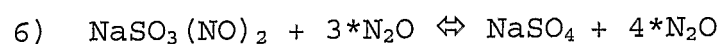
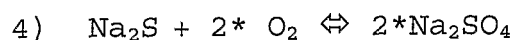
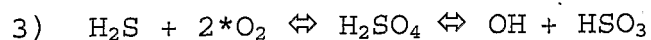
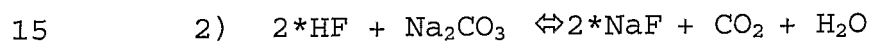
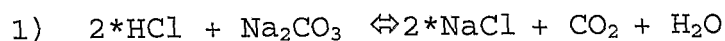
In addition to the SO_x reactions there are additionally NO_x reactions occurring in the injection phase which include the following:

- 15 1) $\text{Na}_2\text{SO}_3 + 2*\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2*\text{NaNO}_3 + \text{SO}_3(\text{g})$
- 2) $\text{Na}_2\text{SO}_3 + 2*\text{NO}(\text{g}) + 2*\text{O}_2(\text{g}) \rightleftharpoons 2*\text{NaNO}_3 + \text{SO}_3(\text{g})$
- 3) $\text{Na}_2\text{SO}_3 + 2*\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2*\text{NaNO}_2 + \text{SO}_3(\text{g})$
- 4) $\text{Na}_2\text{CO}_3 + 2*\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2*\text{NaNO}_3 + \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
- 20 5) $2*\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2*\text{NO}_2(\text{g})$
- 6) $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_3(\text{g})$
- 7) $2*\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
- 8) $\text{N}_2\text{O}_3(\text{g}) + \text{H}_2\text{O} \rightleftharpoons 2*\text{HNO}_2$
- 9) $\text{N}_2\text{O}_3(\text{g}) + 2*\text{NaOH} \rightleftharpoons 2*\text{NaNO}_2 + \text{H}_2\text{O}$

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10 In terms of the reactions that occur in the wet scrubber, many of the NO_x reactions indicated above occur in the wet scrubbing phase as well as the following acid gas reactions:



As discussed herein previously, the oxidant loops where oxidant is injected into the wet scrubber by points 58 and 60. Typical of the reactions that will occur from an oxidation point of view include the following:

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- 1) $O(g) + O_2(g) \rightleftharpoons O_3(g)$
- 2) $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$
- 3) $2*NO(g) + O_3(g) \rightleftharpoons N_2O_5(g)$
- 4) $2*NO(g) + O_2(g) \rightleftharpoons 2*NO_2(g)$
- 5) $2*NO_2(g) + O_3(g) + H_2O \rightleftharpoons 2*HNO_3(g) + O_2(g)$
- 6) $NO(g) + NaClO \rightleftharpoons NaCl + NO_2(g)$
- 7) $H_2S + 4*NaClO \rightleftharpoons 4*NaCl + H_2SO_4$
- 8) $H_2S + H_2O_2 \rightleftharpoons S + 2*H_2O$
- 9) $4*NO(g) + 3*NaClO_2 + 4*NaOH \rightleftharpoons 4*NaNO_3 + 3*NaCl +$
 10 $2*H_2O$
- 10) $4*NO_2(g) + NaClO_2 + 4*NaOH \rightleftharpoons 4*NaNO_3 + NaCl +$
 $2*H_2O$
- 11) $2*Na_2SO_3 + NaClO_2 \rightleftharpoons 2*Na_2SO_4 + NaCl$
- 12) $3*H_2O_2 + 2*NO(g) \rightleftharpoons HNO_3 + 2*H_2O$
- 13) $H_2O_2 + HNO_2 \rightleftharpoons HNO_3 + H_2O$

As a particular convenience, the dry injection scrubbing operation as well as the wet scrubbing operation are particularly useful in reducing other air toxic compounds present in the flue gas.

20 Based on the Environmental Protection Agency in the United States, the listed air toxic compounds include the following:

Acetaldehyde

Acetamide

25 Acetonitrile

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Acetophenone

2-Acetylaminofluorene

Acrolein

Acrylamide

5 Acrylic acid

Acrylonitrile

Allyl chloride

4-Aminobiphenyl

Aniline

10 o-Anisidine

Asbestos

Benzene (including benzene from gasoline)

Benzidine

Benzotrichloride

15 Benzyl chloride

Biphenyl

Bis(2-ethylhexyl)phthalate (DEHP)

Bis(chloromethyl) ether

Bromoform

20 1,3-Butadiene

Calcium cyanamide

Captan

Carbaryl

Carbon disulfide

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Carbon tetrachloride

Carbonyl sulfide

Catechol

Chloramben

5 Chlorodane

Chlorine

Chloroacetic acid

2-Chloroacetophenone

Chlorobenzene

10 Chlorobenzilate

Chloroform

Chloromethyl methyl ether

Chloroprene

Cresol/Cresylic acid (mixed isomers)

15 o-Cresol

m-Cresol

p-Cresol

Cumene

2,4-D, salts and esters (2,4-Dichlorophenoxyacetic

20 Acid)

DDE (1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene)

Diazomethane

Dibenzofuran

1,2-Dibromo-3-chloropropane

25 Dibutyl phthalate

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- 1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
Dichloroethyl ether (Bis[2-chloroethyl]ether)
1,3-Dichloropropene
5 Dichlorvos
Diethanolamine
Diethyl sulfate
3,3'-Dimethoxybenzidine
4-Dimethylaminoazobenzene
10 N,N-Dimethylaniline
3,3'-Dimethylbenzidine
Dimethylcarbamoyl chloride
N,N-Dimethylformamide
1,1-Dimethylhydrazine
15 Dimethyl phthalate
Dimethyl sulfate
4,6-Dinitro-o-cresol (including salts)
2,4-Dinitrophenol
2,4-Dinitrotoluene
20 1,4-Dioxane (1,4-Diethyleneoxide)
1,2-Diphenylhydrazine
Epichlorohydrin (1-Chloro-2,3-epoxypropane)
1,2-Epoxybutane
Ethyl acrylate

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- Ethylbenzene
- Ethyl carbamate (Urethane)
- Ethyl chloride (Chloroethane)
- Ethylene dibromide (Dibromoethane)
- 5 Ethylene dichloride (1,2-Dichloroethane)
- Ethylene glycol
- Ethyleneimine (Aziridine)
- Ethylene oxide
- Ethylene thiourea
- 10 Ethylidene dichloride (1,1-Dichloroethane)
- Formaldehyde
- Heptachlor
- Hexachlorobenzene
- Hexachlorobutadiene
- 15 1,2,3,4,5,6-Hexachlorocyclohexane (all stereo isomers,
including lindane)
- Hexachlorocyclopentadiene
- Hexachloroethane
- Hexamethylene diisocyanate
- 20 Hexamethylphosphoramide
- Hexane
- Hydrazine
- Hydrochloric acid (Hydrogen Chloride)
- Hydrogen fluoride (Hydrofluoric acid)
- 25 Hydroquinone

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- Isophorone
- Maleic anhydride
- Methanol
- Methoxychlor
- 5 Methyl bromide (Bromomethane)
- Methyl chloride (Chloromethane)
- Methyl chloroform (1,1,1-Trichloroethane)
- Methyl ethyl ketone (2-Butanone)
- Methylhydrazine
- 10 Methyl iodide (Iodomethane)
- Methyl isobutyl ketone (Hexone)
- Methyl isocyanate
- Methyl methacrylate
- Methyl tert-butyl ether
- 15 4,4'-Methylenebis(2-chloroaniline)
- Methylene chloride (Dichloromethane)
- 4,4'-Methylenediphenyl diisocyanate (MDI)
- 4,4'-Methylenedianiline
- Naphthalene
- 20 Nitrobenzene
- 4-Nitrobiphenyl
- 4-Nitrophenol
- 2-Nitropropane
- N-Nitroso-N-methylurea

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- N-Nitrosodimethylamine
- N-Nitrosomorpholine
- Parathion
- Pentachloronitrobenzene (Quintobenzene)
- 5 Pentahlorophenol
- Phenol
- p-Phenylenediamine
- Phosgene
- Phosphine
- 10 Phosphorus
- Phthalic anhydride
- Polychlorinated biphenyls (Aroclors)
- 1,3-Propane sultone
- beta-Propiolactone
- 15 Propionaldehyde
- Propoxur (Baygon)
- Propylene dichloride (1,2-Dichloropropane)
- Propylene oxide
- 1,2-Propylenimine (2-Methylaziridine)
- 20 Quinoline
- Quinone (p-Benzoquinone)
- Styrene
- Styrene oxide
- 2,3,7,8-Tetrachlorodibenzo-p-dioxin

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- 1,1,2,2-Tetrachloroethane
Tetrachloroethylene (Perchloroethylene)
Titanium tetrachloride
Toluene
5 Toluene-2,4-diamine
2,4-Toluene diisocyanate
o-Toluidine
Toxaphene (chlorinated camphene)
1,2,4-Trichlorobenzene
10 1,1,2-Trichloroethane
Trichloroethylene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triethylamine
15 Trifluralin
2,2,4-Trimethylpentane
Vinyl acetate
Vinyl bromide
Vinyl chloride
20 Vinylidene chloride (1,1-Dichloroethylene)
Xylenes (mixed isomers)
o-Xylene
m-Xylene
p-Xylene

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- Antimony Compounds
- Arsenic Compounds (inorganic including arsine)
- Beryllium Compounds
- Cadmium Compounds
- 5 Chromium Compounds
- Cobalt Compounds
- Coke Oven Emissions
- Cyanide Compounds
- Glycol ethers
- 10 Lead Compounds
- Manganese Compounds
- Mercury Compounds
- Fine mineral fibers
- Nickel Compounds
- 15 Polycyclic Organic Matter
- Radionuclides (including radon)
- Selenium Compounds

In conclusion, by combining dry injection and wet scrubbing operations, the concentrations of SO₂ and NO_x were reduced immediately primarily due to their respective chemical reactions with NaHCO₃. Other sorbents clearly will also provide effectiveness including the calcium and magnesium based sorbents such as calcium carbonate, calcium bicarbonate, calcium hydroxide, magnesium carbonate, magnesium bicarbonate, magnesium hydroxide or any combination of these.

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Reference to U.S. Patent Nos. 6,143,263 and 6,303,083 may be made for other examples in SO_x removal.

The scrubber proved very effective at removing NO₂ which can account for a significant portion of the overall
5. NO_x; the scrubber was also effective in removing sulfuric compounds resulting in near zero SO₂ emission.

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CLAIMS:

1. A method of scrubbing SO_x and NO_x compounds from a flue gas stream, characterized in that said method comprises:

a dry injection scrubbing operation and a wet scrubbing operation, said dry injection scrubbing operation including:

contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent for removing substantially all of the SO_x and a large amount of NO_x compounds present in said stream; and

said wet scrubbing operation including:

contacting said stream to remove any residual SO_x and NO_x compounds remaining in said stream.
2. The method as set forth in claim 1, characterized in that said sorbent is a sodium based sorbent selected from the group consisting of sodium bicarbonate, sodium carbonate, sodium hydroxide, or combinations thereof.
3. The method as set forth in claim 1, characterized in that said sorbent is a calcium based sorbent selected from the group consisting of calcium carbonate, calcium bicarbonate, calcium hydroxide and combinations thereof.

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4. The method as set forth in claim 1, characterized in that said sorbent is a magnesium based sorbent selected from the group consisting of magnesium carbonate, magnesium bicarbonate, magnesium hydroxide and combinations thereof.
5. The method as set forth in claim 1, characterized in that said sorbent comprises a combination of sodium, magnesium and calcium sorbents.
6. The method as set forth in claim 1, characterized in that said dry injection scrubbing operation produces sodium sulfate, sodium sulfite, sodium fluoride, sodium chloride, sodium nitrite, sodium carbonate and/or sodium nitrate.
7. The method as set forth in claim 1, characterized in that said SO_x and NO_x compounds include SO_2 , SO_3 , NO_2 , N_2O_3 , N_2O_5 , N_xO_y and dimers thereof.
8. The method as set forth in claim 1, characterized in that said method further includes the step of recirculating unreacted sorbent for use in said wet scrubbing operation.
9. The method as set forth in claim 1, characterized in that said method further includes the step of oxidizing said flue gas stream.
10. The method as set forth in claim 9, characterized in that said method further includes the step of oxidizing said stream subsequent to treatment in

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either or both of said wet scrubbing operation and said dry scrubbing operation.

11. The method as set forth in claim 1, characterized in that said step of oxidizing includes the use of an oxidant selected from the group consisting of hydrogen peroxide, ozone, NaClO_x , where x is 1 through 4, or a combination thereof.
12. The method as set forth in claim 1, characterized in that said method further includes the step of reducing air toxic compounds present in said flue gas by reaction with said dry injection scrubbing operation and said wet scrubbing operation and oxidant addition.
13. A method of scrubbing SO_x and NO_x compounds from a flue gas stream, characterized in that said method comprises:
 - a dry injection scrubbing operation and a wet scrubbing operation, said dry injection scrubbing operation including:
 - contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent for removing substantially all of the SO_x and a large amount of NO_x compounds present in said stream;
 - said wet scrubbing operation including:
 - contacting said stream to remove any residual SO_x and NO_x compounds remaining in said stream;
 - and

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recirculating unreacted sorbent to said wet scrubbing operation.

14. The method as set forth in claim 13, characterized in that said method further includes the step of oxidizing said stream.
15. The method as set forth in claim 13, characterized in that said sodium based sorbents are selected from the group consisting of sodium based sorbents, calcium based sorbents, magnesium based sorbents and combinations thereof.
16. A method of scrubbing SO_x and NO_x compounds from a flue gas stream, characterized in that said method comprises:
 - a dry injection scrubbing operation and a wet scrubbing operation, said dry injection scrubbing operation including:
 - contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent for removing substantially all of the SO_x and a large amount of NO_x compounds present in said stream; and
 - said wet scrubbing operation including:
 - scrubbing said stream from said dry injection scrubbing operation in the presence of an oxidant to remove any residual SO_x and NO_x compounds remaining in said stream.

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17. The method as set forth in claim 16, characterized in that said method further includes the step of recirculating unreacted sorbent to said wet injection scrubbing operation.
18. The method as set forth in claim 16, characterized in that said oxidant is selected from the group consisting of hydrogen peroxide, ozone, NaClO_x , where x is 1 through 4, or a combination thereof.
19. The method as set forth in claim 16, characterized in that said stream from said dry injection scrubbing operation is exposed to oxidant.
20. The method as set forth in claim 16, characterized in that said stream from said dry injection scrubbing process produces sodium sulfate, sodium sulfite, sodium fluoride, sodium chloride, sodium nitrite, sodium carbonate and/or sodium nitrate.
21. A method of scrubbing SO_x and NO_x compounds from a flue gas stream, characterized in that said method comprises:
 - a wet injection scrubbing operation and a wet scrubbing operation, said wet injection scrubbing operation including:
 - contacting a flue gas stream containing SO_x and NO_x compounds with a sorbent solution for removing substantially all of the SO_x and a large amount of NO_x compounds present in said stream; and

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said wet scrubbing operation including:

contacting said stream to remove any residual SO_x
and NO_x compounds remaining in said stream.

22. The method as set forth in claim 21, characterized in that said stream from said wet scrubbing operation is polished in a wet electrostatic precipitator.
23. The method as set forth in claim 16, characterized in that said stream from said wet scrubbing operation is polished in a wet electrostatic precipitator.
24. The method as set forth in claim 13, characterized in that said stream from said wet scrubbing operation is polished in a wet electrostatic precipitator.
25. The method as set forth in claim 22, characterized in that said method further includes removing other air toxins and fine particulate matter in said electrostatic precipitator.