

## Critical Analysis of Harmful Gases from Flue Gas

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The invention provides a wet, regenerable scrubbing process using ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution to remove acid anhydride moiety gases, and trace amounts of hydrogen chloride gas (HCl) and hydrogen fluoride (HF) gas in a gas-liquid contacting reactor. In particular, the invention uses "aqua ammonia" or an aqueous ammonia scrubbing liquor such as  $[\text{NH}_3(\text{aq})/\text{ammonium hydroxide } (\text{NH}_4\text{OH})]$  to extract certain effluent compounds via acid-base or neutralization reactions. Generally, an effluent gas is subjected to chemical scrubbing with aqueous ammonia or some other ammonia-containing compound in a gas-liquid contactor reactor or a scrubber to remove gaseous acid anhydride moieties. The chemical scrubbing produces ammonium salts of the conjugate bases of the acid anhydride moieties. Thermal regeneration of the ammonia scrubbing liquor occurs in an adjacent vessel or remotely.

**Key words:** Harmful gases, Flue gas, regenerable scrubbing process.

The exhaust gas of a medium-speed four-stroke Diesel engine is composed of numerous of constituents. These come either from the combustion air and fuel used, or they are reaction products which form during the combustion process. Only some of these are to be considered as pollutants<sup>1-2</sup>.

The typical composition of the exhaust gas of an MAN B&W four-stroke Diesel engine is shown in table 1.

### Exhaust gas components

- 1) With sulphur content in the fuel oil of 3% by weight as it is typical for marine fuels.
- 2) Total  $\text{NO}_x$  emission calculated as  $\text{NO}_2$ .
- 3) Pure soot, without ash or any other particle-borne components.

According to the present state of knowledge, the following of these constituents are considered to be harmful to the environment.

### Carbon dioxide $\text{CO}_2$

$\text{CO}_2$  actually is entirely nontoxic and is a product of combustion of all fossil fuels. It is now considered to be one of the main causes of the greenhouse effect. A reduction of the  $\text{CO}_2$  emission can only be achieved by improving the engine efficiency or by using fuels containing a lower concentration of carbon, such as natural gas.

### Sulphur oxides $\text{SO}_x$

Sulphur oxides are formed by the combustion of the sulphur contained in the fuel. They are one of the main causes of acid rain. The sulphur oxide emission is primarily influenced by the amount of sulphur contained in the fuel used. Much less influence can be taken by the fuel consumption of the engine. The major part (90 %) of sulphur oxides contained in the exhaust gas of Diesel engines is  $\text{SO}_2$ .

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**Nitrogen oxides  $\text{NO}_x$  (No,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ )**

Nitrogen oxides, which are generally referred to as  $\text{NO}_x$ , in the case of internal combustion engines comprise nitrogen monoxide NO (colorless, water-insoluble gas), nitrogen dioxide  $\text{NO}_2$  (a reddish-brown gas, highly toxic) and dinitrogen monoxide  $\text{N}_2\text{O}$  (laughing gas, a colorless gas formerly used as an anesthetic). Nitrogen oxides, together with the sulphur oxides, are the main causes of acid rain. They also contribute essentially to ozone formation in the air at ground level. The high temperatures and pressures produced in the combustion chamber of an internal combustion engine stimulate the nitrogen contained in the air and also in some fuel grades (such as heavy fuel oil) to react with the oxygen of the combustion air. In this reaction mechanism, the formation of nitrogen oxides increases more than proportionally with rising temperatures.

The  $\text{NO}_x$  forming during the combustion process in a Diesel engine is almost entirely NO, which to a minor extent oxidizes to  $\text{NO}_2$ , either in the combustion chamber or in the exhaust gas systems downstream (exhaust gas piping, exhaust gas turbocharger); the exhaust gas as leaving the engine therefore generally consists of approx. 95% NO and approx. 5%  $\text{NO}_2$ . To simulate the process of NO oxidation to form  $\text{NO}_2$  in the atmosphere, practically all legislators stipulates that in the calculation of the  $\text{NO}_x$  mass flow emitted, the entire  $\text{NO}_x$  is to be taken as  $\text{NO}_2$ . The  $\text{N}_2\text{O}$  concentration in the exhaust gas of medium-speed Diesel engines is only a few ppm and therefore be neglected from the environmental protection point of view.

**Carbon monoxide CO**

Carbon monoxide is a colorless, highly toxic gas which forms where the combustion of fuels containing carbon proceeds under (possibly local) deficiency of air. In MAN B&W four-stroke Diesel engines, optimization of mixture formation and turbo charging processes successfully reduces the CO content of the exhaust gases, even with poorest quality fuel grades being used, to such a level that even the limits of TA-Luft, the German regulations governing pollution emissions to the air from stationary engine plants, which are among the strictest in the world, can be easily met.

**None - burn hydrocarbons HC**

The hydrocarbons contained in the

exhaust gas are composed of a multitude of various organic compounds. As a whole, however, the HC content of exhaust gases of MAN B&W four-stroke Diesel engines is at a very low level.

**Soot and dust**

Solids contained in the exhaust gas of Diesel engines consist not only of the soot (carbon) resulting from incomplete combustion, but also of dust and ash particles from the fuel, the lube oil, the combustion air and from abrasion products. Although they constitute the main source of visible dark coloration of exhaust gases, soot particles only account a portion of the total dust concentration, depending on the ash content of the fuel and lube oil used.

Suitable for extraction and conversion include, but are not limited to, carbon dioxide ( $\text{CO}_2$ ), sulfur dioxide ( $\text{SO}_2$ ), sulfur trioxide ( $\text{SO}_3$ ), and nitrogen oxides ( $\text{NO}_x$ ). However, other extraction candidates include hydrogen chloride/hydrochloric acid (HCl) and hydrogen fluoride/hydrofluoric acid (HF). Preferably, some of the gaseous anhydride moieties initially present are oxidized to higher gaseous acid anhydride moieties to improve their reactivity with ammonium hydroxide.

These particular gaseous anhydride moieties to be oxidized include, but are not limited to, sulfur oxides such as sulfur dioxide ( $\text{SO}_2$ ), and nitrogen oxides such as nitrous oxide ( $\text{N}_2\text{O}$ ) and nitric oxide (NO). The oxidation product moieties or higher gaseous acid anhydride moieties include, but are not limited to, sulfur trioxide ( $\text{SO}_3$ ), and nitrogen dioxide ( $\text{NO}_2$ ). The step of converting the acid anhydrides includes reacting the oxidized anhydrides with ammonia-containing compounds<sup>3-4</sup>.

The ammonia-containing compounds are water-soluble compounds selected from the group consisting of aqueous ammonia, ammonium hydroxide, ammonium carbonate, ammonium carbonate solutions, and combinations thereof<sup>5-7</sup>. The removal efficiency of carbon dioxide by aqua ammonia can be as high as 99%, and aqua ammonia's loading capacity for carbon dioxide is greater than unity, and can approach 1.20 kilograms (Kg) of carbon dioxide for each Kg of ammonia. Gaseous ammonia loss into the atmosphere can be minimized by the placement of a mist eliminator in fluid communication with the gas-liquid contactor reactor or scrubber. The mist eliminator comprises

a plurality of heat exchanging surfaces which, when combined with water, provides an exemplary means for eliminating aqueous ammonia from any aerosol secondary stream. Essentially, the water washes out the ammonia in the gaseous phase.

## MATERIALS AND METHODS

The invented process generally comprises the following: flue gas is cooled, passes through a particulate collection device, then is oxidized by strong oxidant prior to entering the gas-liquid contactor reactor<sup>8</sup>. In the oxidizer, lower acid anhydride moieties can be oxidized to higher acid anhydride moieties, e.g., sulfur dioxide (SO<sub>2</sub>) is converted to sulfur trioxide (SO<sub>3</sub>), and nitric oxide (NO) is oxidized to nitrogen dioxide (NO<sub>2</sub>). The contactor reactor temperature is in the range of from about 15° C. to 50° C. for the simultaneous absorption of carbon dioxide (CO<sub>2</sub>), SO<sub>3</sub>, and NO<sub>2</sub>. [5-8] Carbon dioxide, nitrogen dioxide, sulfur trioxide, hydrogen chloride, and hydrogen fluoride react with ammonia or ammonium hydroxide solution in a scrubber to form ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) and/or ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>); ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>); ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>); ammonium chloride (NH<sub>4</sub>Cl); and ammonium fluoride (NH<sub>4</sub>F), respectively, according to Equations through



The ammonium salt products of the neutralization/acid-base reactions can be dewatered by filtration or centrifugation for use as fertilizers, or dried and crystallized. In the alternative, the ammonium bicarbonate formed can

be decomposed to regenerate the ammonia.

There are at least three preferred embodiments of the instant invention. These three embodiments present options as to how to handle the ammonium bicarbonate produced by the instant invention. For the three preferred embodiments described infra, the terms “ingress” and “egress” represent, in part, valves controlling the flow and movement of gas, liquids, and solids. In addition, for all three preferred embodiments, movement of the flue gas is facilitated by one or even two fans. One fan can be an induced draft fan (ID fan) which produces a slight positive pressure. An ID fan is commonly installed in either the chimney inlet in an effluent gas producing plant to force the flue gas to flow upward to exit the smoke stack, or after the particulate control device (PCD) infra to force the flue gas to flow through an acidic gas scrubber (i.e., SO<sub>2</sub>) in a flue gas treatment system<sup>9-11</sup>. A fan can also be placed downstream in each of the three embodiments to provide a slight negative pressure which draws gases out of the systems. The precise locations of the fan(s) will depend upon the operating requirements of the actual plants. Further, pressures throughout the flue gas treatment system will also depend upon the needs of the actual treatment plants.

### General process detail

An exemplary process for the multipollutant control of SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and trace acids such as hydrochloric acid (HCl) and hydrofluoric acid (HF), with integrated reaction and sorption steps, the process designated as numeral. Generally, ambient atmospheric pressures of about 14.7 pounds per square inch absolute (psia) are accommodated in this process, but pressures ranging from approximately 10 psia to 300 psia also are suitable.

First, hot flue gas, containing nitrogen, oxygen, water vapor, and a number of acid anhydride gases such as CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub>, is first cooled by an “air preheater” The air preheater is a heat exchanger that transfers the hot flue gas’s thermal energy to preheat ambient fresh air then used in the ongoing combustion. The flue gas subsequently enters into the system<sup>12</sup>. After being controlled to a predetermined temperature, the flue gas enters a particulate control device (PCD) such as a bag house and/or electrostatic precipitator from which any collected particulate matter is

removed at a suitable point of egress. Ingress into the PCD is controlled via a valve or some other means for controlling ingress into the PCD.

The flue gas subsequently has ingress into an oxidizer reactor into which oxidants also have ingress. The oxidants can be gases or vaporized liquids or radiations initiated and have ingress. The presence of the oxidants in the reactor causes  $\text{SO}_2$  and/or  $\text{NO}_x$  to be oxidized to  $\text{SO}_3$  and/or  $\text{NO}_2$ , respectively. Oxidation of only  $\text{NO}$  may occur. The now-oxidized flue gas, containing  $\text{SO}_3$  and  $\text{NO}_2$ , then enters a first scrubber at a suitable point of<sup>13-15</sup>. In the scrubber, the oxidized moieties contact ammonium hydroxide. The ammonium hydroxide enters the scrubber at a separate point of ingress. In the first scrubber, all acid anhydride gases are neutralized via acid-base/neutralization reactions using ammonium hydroxide sprays or some other means of high volume dispersion of ammonium hydroxide. Preferably, the ammonium hydroxide sprays enter the system via a means to prevent any pressure drop (an exemplary means being a centrifuge spray nozzle), and at a temperature from about 15° C. to 50° C.

The ammonium hydroxide concentration in water can range from about 7 wt. % to 28 wt. %. Nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), and water vapor exit from the first scrubber at an egress point so situated to minimize the likelihood of these gases remixing with the product liquor, i.e., slurry. The ammonium hydroxide is recirculated for the purpose of the neutralization reactions. The products of the neutralization reactions are ammonium salts and exist initially as the slurry of crystalline salts in water. This slurry of salts is dewatered by filtration centrifugation, or some other means which will not decompose the salts. Any resulting supernatant is recycled via a point of ingress to the recirculation loop and the first scrubber. Ultimately, the supernatant is mixed with the contents of the first scrubber reactor. The salts formed from the neutralization reactions contact a crystallizer or some other drying means. The salts have a point of egress, via valves, from the system to be eventually used as fertilizer. All of the salts from the crystallizer can be used as fertilizer. Alternatively, the salts can pass a point of egress, via valve, into regenerator where ammonium bicarbonate (typically greater than 80 wt. % of the slurry/salt mixture) is thermally decomposed to

ammonia and carbon dioxide at a predetermined temperature. Decomposition temperatures of from 35° C. to 80° C. can be used, with 60° C. being a preferred temperature<sup>16-18</sup>.

The other remaining ammonium salts (for example, ammonium chloride, ammonium fluoride, ammonium nitrate, and ammonium sulfate) have a point of egress from the regenerator. The salts from the crystallizer can be used as is for use as a fertilizer, regenerated or a combination of both end uses. The gas mixture of carbon dioxide, ammonia, and water vapor generated by the thermal decomposition of ammonium bicarbonate has ingress into a second scrubber. The second scrubber provides a means for sequestering ammonia entrained in the gas mixture. The sequestering agent in the second scrubber is water-based (e.g., water) with a point of ingress. The final form of the sequestered ammonia is ammonium hydroxide. Liquid-phase ammonium hydroxide subsequently has egress from the second scrubber and is recycled. Due to its much lower solubility in water, carbon dioxide exits the second scrubber from a suitable means of egress and compressed for either storage or subsequent use.

#### **Downstream $\text{CO}_2$ -Processing Detail:**

The instant invention also provides that  $\text{SO}_2$  and  $\text{NO}_x$  are scrubbed with stoichiometric amounts of ammonia with subsequent separate scrubbing of  $\text{CO}_2$  with ammonia. An alternate exemplary process, designated as numeral, for the multipollutant control of  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{CO}_2$ , and trace acids such as hydrochloric acid (HCl) and hydrofluoric acid (HF). [19-20] The process features integrated reaction and sorption steps in which  $\text{SO}_3$  and  $\text{NO}_2$  are simultaneously scrubbed stoichiometrically.  $\text{CO}_2$  is not initially scrubbed. As before, pressures of about 10 psia to 300 psia can be accommodated in this process, with 14 psia to 20 psia typically encountered.

The flue gas, acid anhydride gases, inlet pressure of the flue gas, ingress to the PCD, particulate matter egress, ingress details of flue gas to the oxidizer reactor, oxidants, and ingress details of the oxidants are as aforementioned. As before, the flue gas containing  $\text{SO}_3$  and  $\text{NO}_2$  in the oxidizer, subsequently has ingress to, or otherwise contacts a first scrubber. Ammonium hydroxide has remote ingress into the scrubber in an amount sufficient for stoichiometric reaction of the two

acid anhydrides with the ammonium hydroxide. The carbon dioxide also present is not reacted or "scrubbed" due to the stoichiometric amount of ammonium hydroxide used and the much greater acid strength of  $\text{SO}_3$  and  $\text{NO}_2$  relative to the acid strength of carbon dioxide<sup>21-23</sup>. This difference in acid strengths allows for differentiation between the gases at this point in the process.

A partially treated stream containing carbon dioxide ( $\text{CO}_2$ ), nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), and water vapor have a point of egress from the first scrubber, and a subsequent point of ingress to a second scrubber where the mixture is treated. Ammonium hydroxide also has ingress into this second scrubber. Nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), and water vapor have egress from the second scrubber. As before, the products of the neutralization reactions are ammonium salts and exist as first slurry and second slurry comprising crystalline salts in water. Any ammonium hydroxide not utilized in the neutralization steps is subjected to a first recirculation process and a second recirculation process for subsequent reuse in those respective neutralization steps<sup>24</sup>.

The first slurry contains ammonium chloride, ammonium fluoride, ammonium nitrate, ammonium sulfate, and slight amounts of ammonium bicarbonate. The second slurry contains only ammonium bicarbonate. The first slurry and the second slurry are each dewatered by a first filtration or centrifugation and a second filtration or centrifugation, respectively. The first supernatant and the second supernatant have a first point of egress and a second point of egress from the first filter or centrifuge and the second filter or centrifuge, respectively, and then are recycled via a first point of ingress to the first scrubber and a second point of ingress to the second scrubber, respectively.

The first slurry (ammonium chloride, ammonium fluoride, ammonium nitrate, ammonium sulfate, and possible trace amounts of ammonium bicarbonate) and the second slurry (ammonium bicarbonate) then go through a first crystallizer and a second crystallizer, respectively, to be dried (e.g., a spray dryer or hot air forced circulation can be utilized). After having been dried, the first slurry cake or crystal (now a solid salt mixture) and the second slurry cake or crystal (now solid ammonium bicarbonate) have first egress and second egress,

via flow control means such as a first valve and a second valve, respectively, from the system to be eventually used as fertilizer. An option is that only the second crystal or powder stream from the second scrubber is sent to the regenerator and the first crystal or powder stream from the first scrubber is used directly as fertilizer or visa-versa.

The remaining ammonium salts (ammonium chloride, ammonium fluoride, ammonium nitrate, and ammonium sulfate) exit from the regenerator via a separate means of egress<sup>25</sup>. Gravity can serve as the means for driving the flow of all crystals or powders through valves, into the regenerators, and out of the system. Again as described supra, the gas mixture of carbon dioxide, ammonia, and water vapor generated by the thermal decomposition of ammonium bicarbonate and ammonium carbonate has ingress into and contacts a third scrubber which serves to sequester ammonia. Water, with a point of ingress, is typical for use in the third scrubber. The ammonium hydroxide subsequently has egress from the third scrubber for recycling. Carbon dioxide exits the third scrubber from a different means of egress to be eventually sequestered or used.

In summary, in this second embodiment carbon dioxide ( $\text{CO}_2$ ) is not scrubbed in the first scrubber. The byproducts of the first stage scrubber are primarily ammonium chloride, ammonium fluoride, ammonium nitrate, and ammonium sulfate. Carbon dioxide is absorbed in the second stage scrubber, where ammonium bicarbonate is produced.

#### **Scrubbing of $\text{SO}_3$ and $\text{NO}_2$ With Regeneration of $\text{NH}_3$ and $\text{CO}_2$ from Ammonium Bicarbonate Solution**

The instant invention provides a process such that  $\text{SO}_3$  and  $\text{NO}_2$  are scrubbed with stoichiometric amounts of ammonia with subsequent separate scrubbing of  $\text{CO}_2$  with ammonia. Regeneration of ammonia and carbon dioxide occurs through the heating of the ammonium bicarbonate solution or slurry. The process, designated as numeral, provides multipollutant control of  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{CO}_2$ , and trace acids such as hydrochloric acid (HCl) and hydrofluoric acid (HF). The process comprises integrated reaction and sorption steps in which  $\text{SO}_3$  and  $\text{NO}_2$  are scrubbed stoichiometrically.[26]  $\text{CO}_2$  is not initially scrubbed and ammonia is

recovered downstream by thermal decomposition of an ammonium bicarbonate solution or slurry in water. As before, ambient atmospheric pressures of about 14.7 pounds per square inch absolute (psia) are typically accommodated in this process.

A flue gas, acid anhydride gases, ingress of the flue gas to the PCD, particulate matter egress, ingress of the flue gas to the oxidizer reactor, and ingress of the oxidants to the oxidizer reactor are as aforementioned. As before, the flue gas exit from the oxidizer, with SO<sub>3</sub> and NO<sub>2</sub> present, and subsequently has a point of ingress into a first scrubber<sup>27</sup>. Ammonium hydroxide enters that same first scrubber through a point of ingress. As before, the amount of ammonium hydroxide is such that it allows for stoichiometric reaction of the two acid anhydrides. Any carbon dioxide present is not reacted or “scrubbed” due to the much greater acid strength of SO<sub>3</sub> and NO<sub>2</sub>. As before, carbon dioxide, nitrogen, oxygen, and water vapor exit via a point of egress from the first scrubber, with entry through a subsequent point of ingress to a second scrubber.

Ammonium hydroxide is introduced into the second scrubber through a point of ingress. The contact of the carbon-dioxide containing gas with ammonium hydroxide in the second scrubber results in nitrogen, oxygen, and water vapor exiting the second scrubber via a point of egress. As before, the products of the neutralization reactions (ammonium salts) exist initially as a first slurry and a second solution or slurry of crystalline salts in water. Any residual ammonium hydroxide is recirculated back to the neutralization chambers for reuse via a first recirculation path and a second recirculation path.

The first slurry contains ammonium chloride, ammonium fluoride, ammonium nitrate, and ammonium sulfate, and a possible trace amount of ammonium bicarbonate. The second solution or slurry contains only ammonium bicarbonate or ammonium carbonate. The first slurry is dewatered via a means to effect filtration or centrifugation. Any supernatant, exits from the filter or centrifuge via a point of egress, and is recycled for reuse through a point of ingress back to the first scrubber.

The first salt batch (ammonium chloride, ammonium fluoride, ammonium nitrate, and ammonium sulfate and a possible trace amount of

ammonium bicarbonate) is subjected to a crystallizer (dryer).[28] After having been dried, the first salt batch (now a crystal or powder stream) leaves the system through a point of egress to be eventually used as fertilizer. The second solution or slurry (ammonium bicarbonate) enters, through a point of ingress, into a regenerator wherein the solution or slurry is heated to decompose the ammonium bicarbonate to ammonium hydroxide and carbon dioxide.

The regenerated ammonium hydroxide stream is recycled for carbon dioxide absorption purposes, via a point of ingress back into the second scrubber. As before, the product carbon dioxide from the thermal decomposition of ammonium bicarbonate can be sequestered. Ammonia and carbon dioxide are regenerated from the ammonium bicarbonate solution or slurry by directly heating the slurry in a heater/regenerator up to a temperature of from about 60° C to 80° C.

**RESULTS AND DISCUSSION**

In all three processes described supra, the dewatered slurries of ammonium salts can be sold as fertilizer without the drying or crystallization steps disclosed therewith. Thus, those steps and that equipment can be bypassed or even omitted from the system if needed. A myriad of oxidizing agents are utilized in the invented method, including various chemical and mechanical means. For example, suitable oxidizing agents include, but are not limited to, ozone (O<sub>3</sub>), chlorine dioxide (CO<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and irradiation initiated techniques.

**Table 1.**

Exhaust gas component		Approx . ca
Nitrogen .	N2	75.0
Oxygen. ...	O2	% by vol 12.3
Inert gases	Ar,	0.9
Carbon dioxides	Co2	5.6
Steam. ....	H2O	6.0
Sulphur dioxide	SO2	12.0
Nitrogen oxide		g/kWh 11.0 - 16.0
NO X (NO 2)		0.7
Carbon monoxide	CO	1.2
Hydrocarbons.	HC	0.3
Soot and dust		

The following examples are for illustrative purposes only. Absorption/Regeneration Examples as mentioned below:

A simulated flue gas [15 mole (mol) % CO<sub>2</sub> and 85 mol % nitrogen, N<sub>2</sub>] was utilized in this example. The reactor comprised a double-jacketed glass column packed with structured packing (BX Gauze, Koch Engineering Company, Wichita, Kans.) at 85° F. (29° C.). The flue gas flowed countercurrent to the ammonia solution.

Test results of CO<sub>2</sub> capture by ammonia solution in three different concentrations at 85° F. (29° C.). The packed bed was 21 inches (in) in height. As expected, a higher ammonia concentration gives greater carbon dioxide removal efficiency.

Another series of experiments of an aqua ammonia process for CO<sub>2</sub> capture were conducted, under conditions similar to those for the data in

Table 1, to simulate a steady-state condition under semi-continuous recycle absorption and regeneration operation. Three different solution concentrations were used, 14%, 10.5%, and 7% ammonia by weight (wt.). The procedure involved using a continuous flow of simulated flue gas which contained 15% CO<sub>2</sub> and 85% nitrogen. After the aqua ammonia solution was saturated with flue gas using a bubbler, the absorbent solution was regenerated by heating to separate CO<sub>2</sub> from the CO<sub>2</sub>-rich absorbent solution. The first-time regenerated solution was then used to reabsorb CO<sub>2</sub>. After the second CO<sub>2</sub>-absorption, the aqua ammonia solution was once again regenerated by heating to release absorbed CO<sub>2</sub>.

The absorption/regeneration cycle was repeated for a third time. The CO<sub>2</sub> loading capacity of the original fresh aqua ammonia solution dropped after the first absorption/regeneration

**Table 2.** Solids in the exhaust gas

Fuel		Gases oil	Heavy fuel oil
Ash content, fuel		0.01	0.1
Ash content, lube oil	%	1.5	4.0
Solids in the exhaust gas:			
Soot (carbon)	mg/m <sup>3</sup>	50 (0.30)	50 (0.30)
Fuel ash	(g/kWh)	4 (0.03)	40 (0.25)
Lube oil ash		3 (0.02)	8 (0.04)

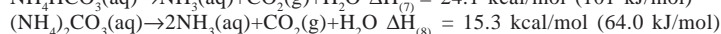
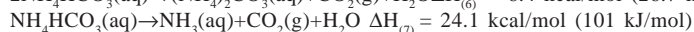
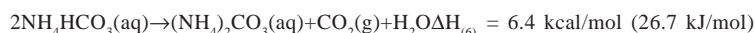
**Table 3.**

S. No	NH <sub>3</sub> conc. wt. %	NH <sub>3</sub> /CO <sub>2</sub> molar ratio	CO <sub>2</sub> % removal efficiency
1	28.0	10.1	97
2	16.9	6.1	94
3	5.6	2.0	70

cycle. However, no detectable CO<sub>2</sub> loading capacity decrease of the solution was observed between the second and third absorption/regeneration cycles. This observation indicated that the simulated testing had reached a steady-state condition in the second and third absorption/regeneration cycles. Thus, an aqua ammonia solution can most likely be used for many

**Table 4.** Steady-state loading capacities for the three aqua ammonia solutions used

S.NO	Aqua Ammonia Concentration (wt. %)	Loading Capacity (g CO <sub>2</sub> /g solution)
1	14	0.068
2	10.5	0.053
3	7	0.04



absorption/regeneration cycles.

The loading capacities compare favorably to current MEA technology. The lowest aqua ammonia CO<sub>2</sub>-loading capacity, at the ammonia concentration of 7 wt. %, is comparable to the CO<sub>2</sub>-loading capacity of 20 wt. % MEA. This demonstrates that more CO<sub>2</sub> can be transferred by a lesser concentration of aqua ammonia solution (and thus a lesser mass of ammonia than of MEA) relative to the performance of aqueous solutions of MEA.

The heat of reaction for the MEA absorption process has been reported to be 20.0 kcal/mol (83.7 kJ/mol). In addition to the heat of reaction and sensible heat requirements, a major contributor to the energy requirements for a MEA process is the heat of vaporization to generate steam to carry the CO<sub>2</sub> overhead in a MEA regenerator. A reflux ratio of 2.0 moles of water (steam) to each mole of CO<sub>2</sub> is common. The energy required to regenerate this amount of steam is an additional 18.9 kcal/mol (79.1 kJ/mol) of CO<sub>2</sub>. Since the regeneration of the aqua ammonia solutions is conducted without this steam energy requirement, an additional energy savings is realized as opposed to the requirements for a MEA-based process. Depending upon which reaction (Equations 6-8) the regeneration step of an absorption/regeneration cycle follows, a 50% to 65% improvement in thermal efficiency is realized by using the aqua ammonia process as opposed to a MEA-based process.

### CONCLUSION

The invented process is relatively simple and quick, generates little or no waste products, thus providing a less costly process with little or no waste disposal problems, and provides useful products. Affordability of the process is offered by the simultaneous removal of all acid gases through a single aqua ammonia process. In addition, the instant invention provides a singular method and device for the capture and separation of gases such as CO<sub>2</sub> and other environmental compounds from effluent gas streams via the use of aqua ammonia or aqueous ammonium hydroxide as a scrubber solution. Further, the gaseous acid anhydrides can be oxidized before any additional treatment occurs.

This feature provides a simpler process at considerable cost savings. The solvent, aqua ammonia or ammonium hydroxide can be regenerated and used for additional neutralization/regeneration cycles thus allowing for additional cost savings. Further, the solvent has a superior loading capacity for greenhouse gases such as carbon dioxide. The absorption products can be used as fertilizer, or, in the instance of ammonium bicarbonate, thermally decomposed to regenerate the ammonia for subsequent reuse in the aqua ammonia scrubbing process, and to regenerate the carbon dioxide for use or storage. This further reduces the cost of the overall air pollution control process. While the invention has been described with reference to details of the illustrated embodiment, these details are not intended to limit the scope of the invention as defined in the appended claims.

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