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NO_x Scrubbing Technology Breakthrough

by
Robert Richardson Ph.D.[*]
Know-NO_x™ LLC

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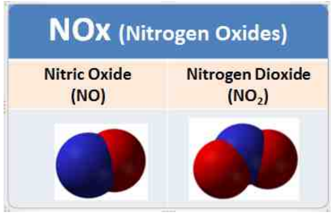
ABSTRACT

This paper presents research findings and practical results that address the treatment of problematic greenhouse gases - nitrogen oxides (NO_x) and sulfur dioxide (SO_2). The newly developed process described here effectively treats both nitric oxide (NO) and nitrogen dioxide (NO_2) in a way that is faster and more effective than other available technologies. This process also simultaneously oxidizes SO_2.



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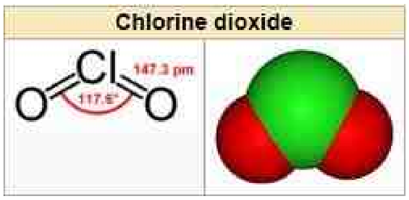
Introduction



An innovative proprietary process,[**] using a different application for chlorine dioxide than has been previously used in NO_x and SO_2 scrubbing, has been developed and is now on the market. This process is innovative because it utilizes chlorine dioxide (ClO_2) in a true gas phase reaction rather than a water-based reaction that occurs in a wet scrubbing process. Gas phase chemistry is much faster than wet scrubbing because it overcomes the wet scrubbing challenge of getting insoluble nitric oxide (NO) into solution. The advantage of using the gas phase reaction makes the equipment less expensive to install and operate than currently available industrial technologies for NO_x treatment. When this gas phase technology is combined with conventional mist or wet scrubbing the operating costs are even lower.

The new patent pending scrubbing process described here is proving to be the optimum solution for ambient temperature waste gas streams containing NO, NO_2 and SO_2, because it has the following attributes:

- Very fast reaction time. This technology allows smaller equipment size and tunable removal efficiency. One can cost effectively tune the removal efficiency from greater than 99% to just above regulatory compliance.
- Very scalable. The process can be applied to contaminated air from a single point source or to contaminated air for an entire facility.
- The process treats both NO_x and SO_2 without additional equipment.
- The technology integrates well with other scrubber / abatement technology, including retrofit and upgrade applications.

Although this process has broad technical applications for a number of other processes, it offers a profound and immediate improvement in the treatment of industrially created NO_x-laden exhaust gas. The process is ideal for exhaust gas treatment from facilities that provide chemical milling, brightening, pickling of metals and other chemical processes that involve nitric acid. There are many ways to treat NO_x, as shown in Table 1. Each has advantages and limitations. This paper will compare and contrast these technologies from the perspective of applicability to the chemical milling industry.

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[*] Corresponding author:
Dr. Robert Richardson
Know-NOx™ LLC
187 E. Warm Springs Rd.
PMB #B233
Las Vegas, NV
E-mail: robert@know-nox.biz

[**] Know-NOx™, Know-NOx™ LLC, 187 E. Warm Springs Rd., Las Vegas, NV.

Table 1 - NO_x treatment options.

	Advantages	Disadvantages
Selective catalytic reduction (SCR)	• Low operating cost	• High equipment cost • Catalyst poisoning requires pretreatment for SO_2, metals, etc. • High operating temperature requires preheating for low temperature NO_x sources • Creates particulates
Wet scrubbing	• Many variations available	• Large multi-stage scrubbers • Creates large amounts of liquid waste
Absorption into water at various pH values	• Low equipment cost	• Only applies to NO_2 • High water usage
Adsorption onto carbon, etc.	• Low equipment cost • Useful for low air volume/low NO_x levels	• High operating cost for other than low airflow/low NO_x levels
Know-NO_x proprietary process	• Rapid reaction = small equipment size • High removal efficiency • Flexible application options • Simultaneously treats SO_2 • Not poisoned by metals or other chemicals in the gas stream	• Limited by 140°F gas temperature unless combined with gas temperature conditioner

Brief orientation on chlorine dioxide (ClO_2)

Chlorine dioxide is an often misunderstood molecule with three different sets of chemical characteristics. The literature, including patents, is frequently not clear about which form of this molecule is used in a specific application.

Table 2 identifies the three types of ClO_2. They all have the same number and types of atoms. The only difference is the charge or lack of charge. For clarity, because all three forms of ClO_2 have been called chlorine dioxide in the literature and because the distinctions between the forms of this molecule are important in NO_x scrubbing, this paper will identify the molecular types as shown in the right column in Table 2.

Table 2 - ClO_2 types.

Preferred IUPAC Name	Ionic charge	Conventional formula	Formula used in this paper
Chlorine dioxide	0	ClO_2	$(ClO_2)^0$
Chlorite	-1	ClO_2^-	$(ClO_2)^-$
Chloryl	+1	ClO_2^+	$(ClO_2)^+$

The chemical differences between the three types are dramatic. True chlorine dioxide, $(ClO_2)^0$, is dramatically more effective at removing NO_x and SO_2 than is chlorite, $(ClO_2)^-$. The difference is due to the fact that $(ClO_2)^0$ is a gas and treats NO_x in the gas phase and $(ClO_2)^-$ is ionic and treats NO_x in water. This is important because NO_x is primarily composed of NO and NO_2, and NO is not very soluble in water.

The $(ClO_2)^-$ ion only exists in water and the NO molecule has very low solubility in water, so it is difficult to get them together. That is why for decades, wet scrubbers for NO_x / NO abatement have involved very large multi-stage equipment.

The $(ClO_2)^0$ and NO_x molecules are gases and they react together effortlessly in a gaseous environment. Therefore, the destruction of NO_x is rapid and can be done in ducting without the need for big scrubbers.

Process chemistry

For decades, the wet scrubbing of NO_x was done by adding sodium chlorite ($NaClO_2$) to the scrubber water. When sodium chlorite is added to water, it creates two ions: $(ClO_2)^-$ and Na^+ as shown in the reaction:

$$NaClO_2 + H_2O \rightarrow Na^+ + (ClO_2)^- \qquad (1)$$

The $(ClO_2)^-$ is utilized in the first of a three-stage wet scrubber as described below.

Typical three-stage NO_x wet scrubbing

Any of several compounds such as $(ClO_2)^-$, O_3 or H_2O_2 reacts with NO to form NO_2 in the first of three or more scrubbing stages. In the second stage, the NO_2 is reacted with sodium hydrosulfide (NaHS) or other compounds plus sodium hydroxide (NaOH). This is effective but creates H_2S gas, an odorous and toxic compound that smells like rotten eggs. In the third stage, the hydrogen sulfide (H_2S) generated in the second stage is removed by scrubbing using NaOH and sodium hypochlorite (NaOCl). Our novel gas phase process overcomes the insolubility problem associated with nitric oxide (NO) and does not use chemicals that generate odorous H_2S so there is no need for all of the equipment associated with a three or more stage scrubbing system. This novel system can be done in ducting alone or in ducting plus a single stage mist scrubber or single stage counter current wet scrubber. The options are explained in Table 3a and 3b below.

Proprietary gas/mist NOx scrubbing

Our single-stage NO_x and SO_2 scrubbing combines easily with other technologies to optimize performance and cost. The process is very versatile.

The core of the technology is described as follows:

$$5NO + 2(ClO_2)^{O} + H_2O \rightarrow 5NO_2 + 2HCl \qquad (2)$$

$$(ClO_2)^{O} + NO_2 + 3H_2O \rightarrow 5HNO_3 + HCl \qquad (3)$$

Note that only three molecules of $(ClO_2)^{O}$ are used to treat five molecules of NO_x.

Deshwal and Lee[1] studied the above equations in bench scale work that utilized a liquid reaction chamber. His work succinctly reports the mass transfer in the absorption of SO_2 and NO_x using aqueous $(ClO_2)^-$ and Cl^-. Richardson[2] expanded upon the Deshwal/Lee work by developing and provisionally patenting a methodology to utilize the equations in gas phase reactions.

Deshwal and Lee[1] also report the simultaneous removal of SO_2 and NO (500 and 350 ppm respectively) at 45°C and pH 3.5. The SO_2 is more reactive and soluble and thus it was oxidized first. The surplus oxidant mix then oxidized the NO to NO_2. The NO_2 absorption efficiency increased with increasing oxidant feed rate. The process provided consistent and reproducible SO_2 and NO_x absorption efficiencies of around 100% and 72% respectively at an oxidant feed rate of 3.045 mmole/min.

Richardson[2] improved the removal efficiency of NO_x by reacting in the gas phase rather than the liquid phase used by Deshwal and Lee. The phase change eliminated the rate of reaction limitations associated with the limited solubility of nitric oxide.

In Richardson's work, both reactions occur in a single gas or mist scrubbing stage. The process can reach 98+% removal efficiencies for NO_x in less than 1.5 sec. The $(ClO_2)^{O}$ is generated separately and introduced as a gas or mist into the industrial waste gas contaminated with NO_x/SO_2. The reaction is sufficiently rapid that it requires no reaction vessel. It can be done in specialized ducting at 2,500 ft./min.

This reaction speed is an important point because it dramatically reduces the cost of scrubbing equipment and opens up new options for scrubber equipment placement. The specialized ducting used for our gas phase scrubbing technology can be placed almost anywhere because it works in any orientation: vertical up, vertical down or horizontal. The process is probably the only NO_x/SO_2 abatement process that does not need a large reaction vessel or series of vessels that uses up valuable space.

The pure gas reactions are faster than the mist reactions, but both are very fast when compared to liquid scrubbing. Although the mist reaction is slightly slower, it has advantages in many applications.

Our technology is packaged with other technologies to optimize the removal efficiency, equipment cost and operating costs. The options are described in Table 3 (a and b).

Table 3(a) - Gas/mist/wet NO_x/SO_2 removal technology treatment options.

Waste gas	Temperature	Process sequence	Notes
NO_x (NO / NO_2) and ambient CO_2	< 140°F	A/B or just A	1
NO_x (NO / NO_2) and high CO_2	< 140°F	A	2
NO_x with high SO_2 content and ambient CO_2	< 140°F	D/E, A and B	3
NO_x with high SO_2 content and high CO_2	< 140°F	D/E and A	---
NO_x with low SO_2 content and ambient CO_2	< 140°F	A and B	---
NO_x with low SO_2 content and high CO_2	< 140°F	A	---
NO_x, particulate and ambient CO_2	< 140°F	H, A and B	4
NO_x, particulate and high CO_2	< 140°F	H and A	---
NO_x / SO_2, particulate and ambient CO_2	< 140°F	H/D, A and B	---
NO_x / SO_2, particulate high CO_2	< 140°F	H/D and A	---
NO_x (NO / NO_2) and ambient CO_2	> 140°F	F/G, A and B	5
NO_x (NO / NO_2) high CO_2	> 140°F	F/G and A	---
NO_x with high SO_2 content and ambient CO_2	> 140°F	F/D, A and B	---
NO_x with high SO_2 content and high CO_2	> 140°F	F/D and A	---
NO_x with low SO_2 content and ambient CO_2	> 140°F	F, A and B	---
NO_x with low SO_2 content and high CO_2	> 140°F	F and A	---
NO_x, particulate and ambient CO_2	> 140°F	F, A and B	---
NO_x, particulate and high CO_2	> 140°F	F and A	---
NO_x / SO_2, particulate and ambient CO_2	> 140°F	F, A and B	---
NO_x / SO_2, particulate and high CO_2	> 140°F	F and A	---

Notes:

1. The "A" process will work just fine but the operating cost is reduced when the "B" second stage is added because the "B" stage treats part of the NO_x with less expensive chemicals.
2. Only the "A" process is used when high CO_2 concentrations are present in the waste gas; if the "B" second stage were used there would be excessive NaOH consumption due to the high CO_2 concentration in the waste gas.
3. The "A" process effectively treats SO_2 and it is ideal when there are low SO_2 concentrations in the waste gas, but it is not an economical process for medium or high SO_2 concentrations.
4. Spray towers rely primarily on particle collection by impaction. Therefore, they have high collection efficiencies for coarse PM. Typical removal efficiencies for a spray tower can be as great as 90% for particles larger than 5 µm. Removal efficiencies for particles from 3 to 5 µm in diameter range from 60 to 80%. Below 3 µm, removal efficiencies decline to less than 50% (Mussatti and Hemmer[3]).
5. Evaporative cooling is applicable for cooling up to but not exceeding the dew point. The "A" process requires water so high moisture in the waste gas is an advantage up to the point where condensation adversely influences the gas/mist chemistry.

Although the NOx reaction can be done in a single gas phase as described in Equations 2 and 3, the use of gas phase Equation 2 combined with a second stage mist scrubber or wet scrubber reaction described in Equation 4 provides lower operating costs. Operating costs are an important consideration in the selection of a NO_x abatement process. We recognize this and have developed a cost effective second stage scrubbing process that utilizes less expensive alkaline chemicals and oxidants to treat part of the NO_x. This second stage is dependent on the proprietary first stage reaction (Item "A" in Table 3(b)) to equalize the ratio of NO and NO_2 in the waste gas stream.

The second stage technology (Items "B" &"C" in Table 3(b)) fundamentally utilizes the stoichiometry shown in Equation 4 below.

$$2NaOH + NO_2 + NO \rightarrow 2NaNO_2 + H_2O \qquad (4)$$

Table 3(b) - Key to the Table 3(a) process sequence.

Key	Treatment	Description
A	NO_x / SO_2	Gas/Mist Know-NO_x™ single stage reaction in specialized ducting. Effectively treats NO_x in concentrations from 10 ppm to 60,000 ppm
B	NO_x (NO/NO_2)	2nd stage Know-NO_x™ mist reaction using NaOH and a proprietary oxidizer (Must follow "A" above).
C	NO_x (NO/NO_2)	2nd stage Know-NO_x™ packed bed wet scrubber using NaOH and a proprietary oxidizer (Must follow "A" above).
D	SO_2	Mist type reaction chamber with NaOH. Can be combined with "F and H" in same vessel.
E	SO_2 (high)	Conventional SO_2 treatment like lime, NaOH wet scrubbing and others.
F	Temp >140°F	Mist cooling where humidity is ambient or less. Can be combined with "D and H" in the same vessel.
G	Temp >140°F	Heat exchanger where heat is needed for other processes or humidity is high.
H	Particulate	Mist with condensation and demister device. Can be combined with "D and F" in same vessel.

This reaction is dramatically enhanced by the addition of one of several oxidants and only applies to NO_x mixes with equal quantities of NO and NO_2, as found by Kuropka.[4]

Bench scale research by Kuropka[4] determined that the reaction rate and efficiency of the reaction in Equation 4 is dramatically influenced by the presence of less than stoichiometric concentrations of different oxidants. It was also found that different basic compounds have varying rates of NO_x adsorption. This research was selectively confirmed in both pilot and partial full scale applications by Richardson.[2] In addition to confirming the work by Kuropka, Richardson's work developed new ways to effectively create the requisite balance of the NO/NO_2 in the waste gas stream through patent pending gas/mist phase reactions between $(ClO_2)^O$ and NO_x. Richardson's work studied the applications for the reaction in Equation 4 with varying oxidants, gas velocities and spray densities in both mist scrubber and packed bed scrubber applications.

Kuropka's research is supported by earlier work. Studies on the absorption of NO_x by alkaline solutions were made by Atroscenko[5] and later confirmed by Glowinski, *et al.*[6] It was found that different alkaline solutions have varying rates of NO_x adsorption. Kuropka's research[7,8] established a sequence of activities of alkaline solutions used for the absorption of NO_x.

$$KOH > NaOH > NH_4OH > Na_2CO_3 > K_2CO_3 > (NH_4)_2CO_3 \qquad (5)$$

Kuropka's research which was based on a foundation of previous work, also focused on improving the level of oxidation of NO_x by absorption and simultaneous oxidation of NO_x with compounds that easily release oxygen in the liquid phase, such as sodium hypochlorite (NaOCl),[7,8] sodium chlorite ($NaClO_2$),[9,10] calcium hypochlorite ($Ca(OCl_2)$,[11] potassium permanganate ($KMnO_4$), potassium dichromate ($K_2Cr_2O_7$)[7,8,10] and hydrogen peroxide (H_2O_2).[7,8,12]

Kuropka's bench scale research focused on the adsorption of NO_x by NaOH with varying concentrations of oxidants between 1 and 10 wt% of the NaOH, and oxidants spray density between 5 and 40 m^3/m^2hr with gas velocities between 0.1 and 1 m/sec. The conclusion is that the adsorption of NO_x varies between 95% and 75%. The best results were at the slower gas velocities and higher spray densities.

The different oxidants also influenced the NO_x adsorption efficiency as shown:

$$H_2O_2 > NaOCl > KMnO_4 \qquad (6)$$

The research addressed to perfecting the NO_x adsorption according to the reaction in Equation 4 with less than stoichiometric concentrations of oxidants is only useful for scrubbing NO_x in waste gas with ambient levels of CO_2. Waste gas with elevated levels of CO_2 will utilize large quantities of NaOH or other alkaline material in reactions with the CO_2.

The second stage technology (Items "B" and "C" in Table 3(b)) can be done in mist phase or wet scrubber. This option provides an advantage in retrofit applications that already have a wet scrubber. In many cases the first stage reaction can be done in modified ducting that leads to the existing wet scrubber. The mist type second stage produces less liquid waste than a wet scrubber and that is an advantage in some locations where liquid waste disposal is a problem.

The pure gas reactions described in Equations 2 and 3 are faster than the mist reactions described in Equation 4, but both are very fast when compared to liquid scrubbing using Equation 4.

In industrial waste gas with ambient levels of CO_2, the use of this second stage technology reaction based on the reaction in Equation 4 can save more than half the cost of treating the NO_x with only the first stage reaction (Item "A" in Table 3(b)) because NaOH is considerably less expensive than the sodium chlorite ($NaClO_2$) or sodium chlorate ($NaClO_3$) used to make $(ClO_2)^O$ required for the first stage NO_x scrubbing methodology (Item "A" in Table 3(b)).

Tunable removal efficiency is another advantage of our innovative technology. It is available because, when using our methodology, Equations 2 and 3 are very fast. Removal efficiency is directly related to the amount of time available for a reaction (reaction residence time) and rate of the reaction. The faster the reaction, the more complete the oxidation will be in a given reaction residence time. In conventional applications, there are economic limitations imposed by vessel size and number of scrubbing stages. These directly impact maximum NO_x removal efficiency. Conventional NO_x scrubbing processes, both wet chemistry and selective catalytic reduction (SCR), require multiple scrubbing stages to reach high NO_x removal efficiency. Wet scrubbing reactions are so slow that they require large scrubbing vessels to reach even 80% oxidation NO_x. The speed of our first stage process (Item "A" in Table 3(b)) eliminates economic constraints associated with high NO_x removal efficiency. A reaction vessel can be built that has the reaction residence time required for 98+% NO_x removal efficiency and then detuned to provide only the currently required removal efficiency. If and when additional removal efficiency is desired or required, the same equipment can be re-tuned to meet that new requirement. The client can reduce operating costs by only generating enough $(ClO_2)^O$ to meet current requirements.

Our new technology is very scalable and responsive. Most abatement technologies are designed to be continuously operated at essentially the same removal potential at all times irrespective of variability in the rate of NO_x/SO_2 production. Our gas/mist technology is not limited to "always on" operation. Wet scrubbers recirculate or spray a liquid into a reaction chamber(s). Packed bed scrubbers recirculate a liquid over a packing bed(s) that is stored in a sump. Oxidants are added to the recirculated liquid and the addition rate is controlled by sensors such as for oxidation-reduction potential (ORP) and pH. The control system for wet scrubbers is designed to maintain a constant level of oxidants in the recirculated liquid. This methodology is not responsive to abrupt changes in NO_x/SO_2 loading in the industrial waste gas and utilizes oxidants even when NO_x is not present in the waste gas stream. Mist/gas phase type scrubbers and SCR scrubbers can be responsive to changes in the NO_x concentration of industrial waste gas because sensors adjust the rate of oxidants and other chemicals added to the waste gas stream in response to real time concentrations of NO_x in the waste gas. Our new technology has a further advantage over the SCR because it does not have a catalyst that can be contaminated or "poisoned" by metals or other chemicals in the industrial waste gas stream.

Conclusion

The present study reports on breakthroughs in the treatment of NO_x in industrial waste gas when scrubbed with $(ClO_2)^O$ in a gas/mist phase reaction. This work expands upon work done by Deshwal and others done in liquid phase. The gas/mist phase reaction environment produces NO_x removal efficiencies above 90% in less than 1.5 sec.

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About the author

Dr. Robert Richardson recently celebrated his 25th year in environmental air quality problem solving as president of Pacific Rim Design & Development (PRDD). A strong proponent of process development and applied research resulted in the development of eight patents for process chemistry and technological innovations for air quality control equipment. Dr. Richardson has a reputation as a leading problem solving expert for industry and government when conventional air quality solutions don’t work. In addition to his duties at PRDD, Dr. Richardson formed Know-NOx LLC in 2011 as the vehicle for the deployment of an innovative technology he developed that provides essentially 100% NO_x abatement in a cost effective and “green” way. Robert has B.S., M.S. and Ph.D. degrees in chemistry with additional training in business, engineering and construction. Robert proudly holds a general contractors license which allows him to manage or deliver complete abatement solutions when required.