

Controlling NO_x Emission from Post-blast Process Gases

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Abstract

This study investigates effect of the pH on nitric oxides (NO_x) removal. A spray tower has been used to study the absorption of nitrogen oxides in both acidic and alkaline solution of sodium chlorite (NaClO₂). Sodium chlorite was used as an oxidant in order to oxidise NO to NO₂, which is highly soluble in aqueous phase. NO was oxidized to NO₂ followed by NO₂⁻ and ClO₂ to ClO₂⁻ in liquid phase respectively. The latter was found to be reduced to Cl⁻ and ClO⁻. Varying pH of the solution from acidic and alkaline phases, pH (4-12), which is influential in the efficiency of NO_x removal, was studied. According to the experiments carried out in this study, alkaline medium was found to be more reliable than acidic one, and 100% NO with 86% NO_x removal was observed in ambient conditions. The main reason is attributed to hydrolysis of N₂O₄ in higher pH (basic). Experimental results demonstrate the feasibility of the aqueous solution of sodium chlorite for NO_x removal.

Keywords: NO_x removal, Sodium chlorite (NaClO₂), acidity, alkalinity, FT-IR

Introduction

Emission of NO_x has been a main concern for environment owing to its destructive effects (acidic rain e.g.,) on human being, for example, respiratory system and ecosystems [1]. NO_x is mainly attributed to nitric oxide (NO); however, there are other constituents in NO_x such as nitric dioxide (NO₂), and small quantities of N₂O₄ and N₂O₃ due to equilibrium reactions between NO and NO₂. Having said that NO has deteriorating properties on ecosystems, it also contributes in nutrient overload, toxic chemicals production, and global warming [2]. Moreover, NO_x is one of the main ingredients involved in the formation of urban smog, ground-level ozone leading to eutrophication and heart disease; which is why, controlling of NO and NO₂ have come to a sharp focus currently [3]. Nitrogen Oxide (NO) is formed when a fuel is burnt at high temperature, as a combustion process. Road transportation accounts for 61% of NO emission, while industrial activities such as mining, motor vehicles, and electric utilities make up 32% of the pollution. Typically, NO_x is emitted as NO up to 90- 95% by volume; meanwhile, 5-10% of the remaining emits as NO₂. NO is an odourless and colourless gas, therefore, NO₂ causes NO_x to become visible as a pungent reddish-brown gas [4]. Fig.1 shows how the NO_x gas look like after detonation.

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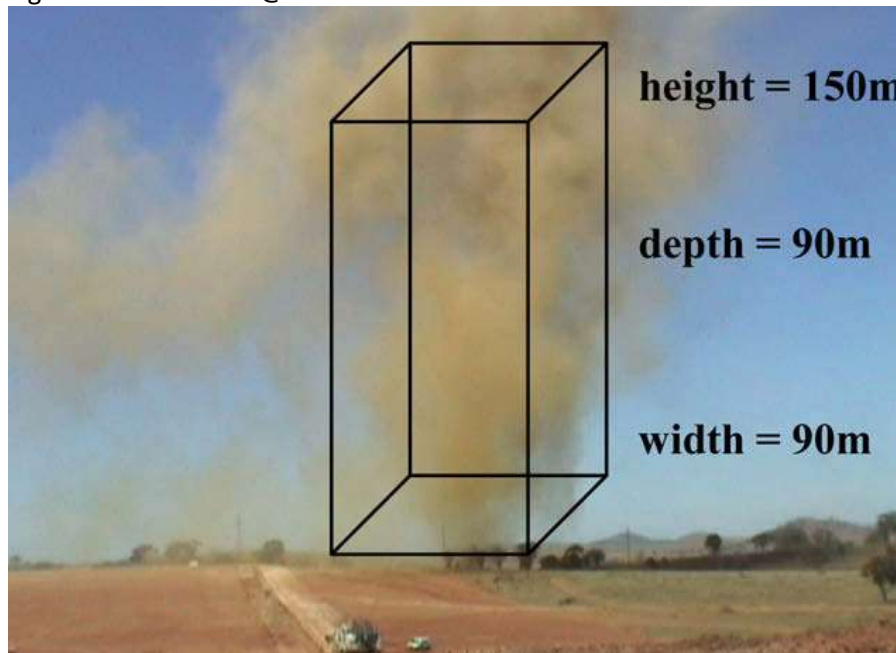
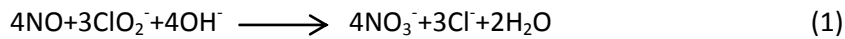


Figure1. Blast plume with estimated dimensions

In this study, our focus will be on other source of NO_x , which is emitted after explosive detonation in mining fields; in other words, NO is oxidized to NO_2 and solubility of NO_x increases due to formation of N_2O_3 and N_2O_4 ; therefore, an oxidant is required to oxidize and absorb NO. Finally, nitrogen oxide is oxidised to nitrite and nitrate depending on composition of the solution. Open-cut coal mining is a widespread technique in countries like Australia and following that a universal explosive called ammonium nitrate/fuel oil (ANFO) is used for this purpose. In recent years, huge attentions have been drawn to the controlling and monitoring of NO/ NO_2 on the basis of the adoption of the Clean Air Act in 1970 due to 20% increase of NO. Therefore, inexpensive and efficient removal techniques were introduced. In other words, selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), flue gas recirculation (FGR), and thermal treatments are amongst them. All these technologies have some disadvantages and capital costs, high temperatures, and disposal problems are to name but a few [3]. In fact, NO_x removal can be divided in two parts which are dry reduction process and wet methods. SCR and SNCR are considered as dry methods, whereas, wet scrubbing absorption, electron beam irradiation or plasma and so on are categorized as wet methods. Amongst the technologies mentioned above, it has been proven that wet scrubbing is the most promising, inexpensive, and efficient removal technique [5]. wet scrubbing absorption can easily dissolve NO_2 in an aqueous phase, but there is a problem with NO whose solubility in aqueous phase is very low; in other words, liquid-phase resistance to mass transfer is sharply increased [1, 6]. In order to overcome this problem, the aqueous phase must contain a strong oxidant which is able to convert NO to NO_2 that is soluble in the aqueous phase. There are known strong oxidants such as hydrogen peroxide (H_2O_2) and peracids, yellow phosphorus (P_4), organic hydroperoxides, sodium chlorite (NaClO_2), potassium permanganate (KMnO_4), sodium hypochlorite, peroxymonosulfate (oxone), and Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) [3]. Having said the available technologies, counter current packed bed scrubbers, spray towers, ejector venturi scrubbers, plate columns, mist scrubbers and even mobile-bed absorbers are used in gas absorption-oxidation techniques [7]. Since this research deals with controlling and capturing NO_x which is emitted and drifted after blast in mining area, mist scrubber or spray towers are categorized in this project. Wet scrubbing has been discouraged by industries in spite of its advantages over other techniques; in other words, cost of chemicals is high along with

their disposal solutions. Therefore, an inexpensive, efficient and environmentally benign chemical should be suggested. Sodium chlorite (NaClO_2) could be one of reliable oxidant used in NO_x removal because it is not only inexpensive but also is stable and its application has already been reported [8]. Also, the absorption of NO_x in NaClO_2 was studied by Sada et.al in their seventies [9-11]. They carried out a series of kinetic investigations in a bubble-column reactor using sodium chlorite. They proved that oxidation power of NaClO_2 rose with decreases in pH value; meanwhile, NO_2 may desorb from the solution if OH^- amount is low. In order to avoid this to happen, additional OH^- is required to fix NO_2 as NO_3^- [8]. The flowing reaction occurs once OH^- is added.



On the top that, other researchers have published their research results which have been summarized in Table 1 [8].

Table 1. Experimental setup, operating conditions, and results of related investigations

Experiment	Reactor Type	[NaClO_2] (M); [NaOH] (M)	p_{NO_x} (ppm)	pH	Gas-liquid contact time (s)	NO_x removal efficiency (%)	Temperature (°C)
1	packed	0.05-0.67	200-900	-	9-18.5	<70	ambient
2	bubble	0.008-0.08	2000	10-14	60	<100	ambient
3	Spray packed	0.037-0.15; 0.008-0.08	300-2000	6.5-12.9	-	<95	ambient
4	packed	0-0.6	290	8-12	11.8	51-84	ambient
5	packed	0.05-0.2; 0-1.0	200-1000	4.5-9.5	1.1	15.9-61.5	ambient
6	Sieve Tray	0.0008-0.0035	200-800	4-6	1	36.6-71.9	ambient

Seda et.al [9] proved that absorption of nitric oxides occurs in a fast reaction regime. In fact, rate constant for the reaction (1) was empirically correlated as follows:

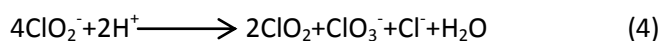
$$k_{mn} = 3.8 \cdot \exp(-3.73[\text{NaOH}]) \quad (2)$$

Where,

OH^- concentration should be in the range of, $0.05 < [\text{NaOH}] < 0.5 \text{ kmol/m}^3$ [9]. Brogren et.al discovered that pH value of solution had a significant impact on the absorption efficiency. It can be explained that major fraction of nitric oxides was absorbed via hydrolysis of N_2O_3 and N_2O_4 [12]. They also suggested reaction (3) as the reaction between NO_2 and ClO_2^- solution.



Acidic medium has also been reported a lot in literature so that some researchers called it better than of alkaline. Deshwal et.al has investigated application of acidic NaClO_2 and has shown that it performed better comparing to alkaline one [13]. It is said that chlorine dioxide gas released from decomposition of sodium chlorite in acidic medium as shown in reaction (4). Plus, it performs as an oxidant, which increases the oxidation of NO in the gas phase [14].



They also assert that oxidative ability of sodium chlorite decreases as pH of solution increases; while, absorptive ability of NaClO_2 increased in alkaline solution [15]. Despite a lot of studies on NO removal in both either acidic medium or alkaline one, this study focuses on impact of various pH

values in ClO_2 and NO_2 formation; moreover, identification and qualification of compounds were discussed. This study is the first one which demonstrates that alkaline medium has more advantages over acidic one with regards to NO_x removal as well as NO_2 and ClO_2 formation. In the meantime, chemistry of reactions was briefly discussed.

Experimental section

Fig.2. shows a schematic diagram of the novel wet scrubber which has been developed for NO_x removal. The spray tower consists of a chamber, a cylindrical chamber, as well as a nebuliser. In other words, nebuliser produces very fine droplets whose size is less than of $10\mu\text{m}$; which means that, process gasses have huge chances to contact the solution. The experimental section is divided to three parts: NO_x gas simulation system, the spray chamber, and reaction product sampling and analysing system. Nitric oxides were obtained from a NO_x cylinder and metered through a mass flow controller (MFC). Nitrogen gas was also applied in order to dilute the mainstream gas (NO_x) as well as production of small droplets by nebuliser. Flow rates of both gasses vary between 0.9-1.1 L/min. Next part considered as absorption chamber in which NO was oxidized and absorbed into the aqueous solution. It performs in the way that those gasses continuously flowed through the system; while, effluent was collected at the bottom of the reactor. Oxidant or liquid solution was pumped upward along with nitrogen gasses through nebuliser. There is reflux glassware at the top of the reactor, which ensured that no liquid passes through the chamber. Furthermore, a Nafion dryer was embedded after the reflux glassware to ensure that all moisture of gas has been removed this was done to protect the gas analyser. Inlet and outlet concentration of NO was measured by 42i-TL TRACE Level NO_x Analyser (Thermo Fisher Scientific Inc.)

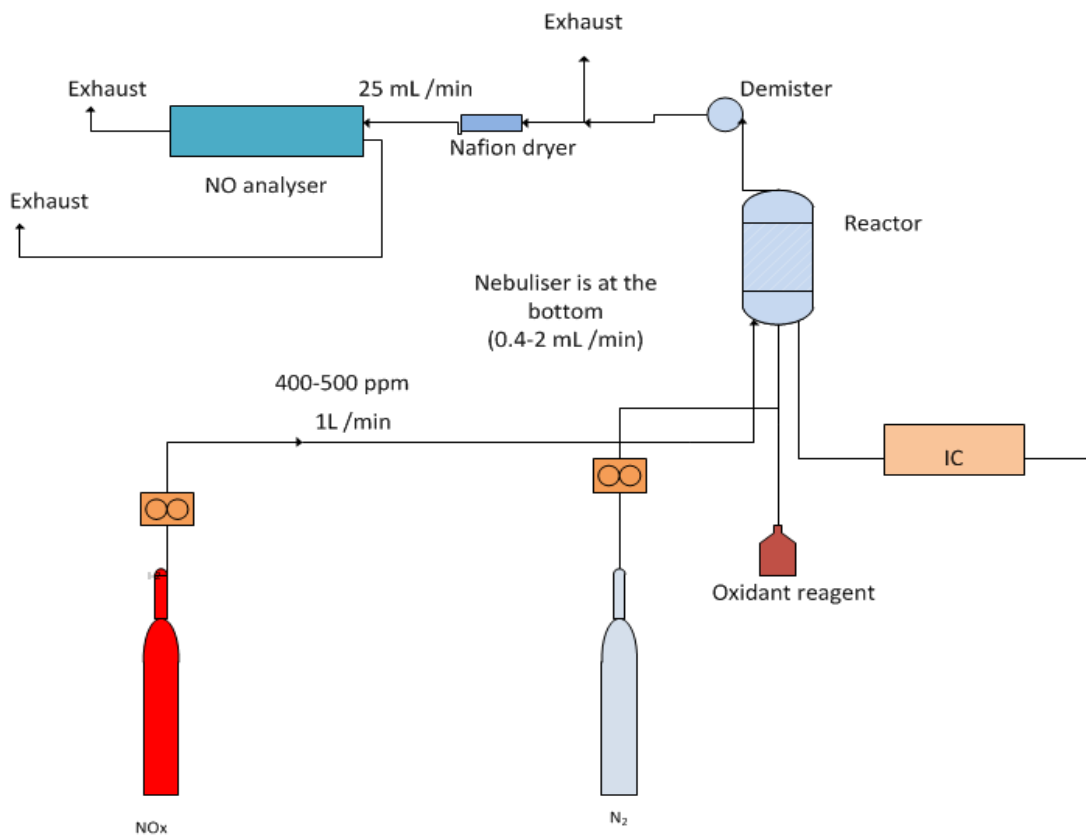


Figure.2. Schematic design of NO_x removal

The SeaSpray concentric nebulizer (Glass Expansion) was used in this experiment to produce fine droplets. The feature of the device was depicted in Fig. 3.

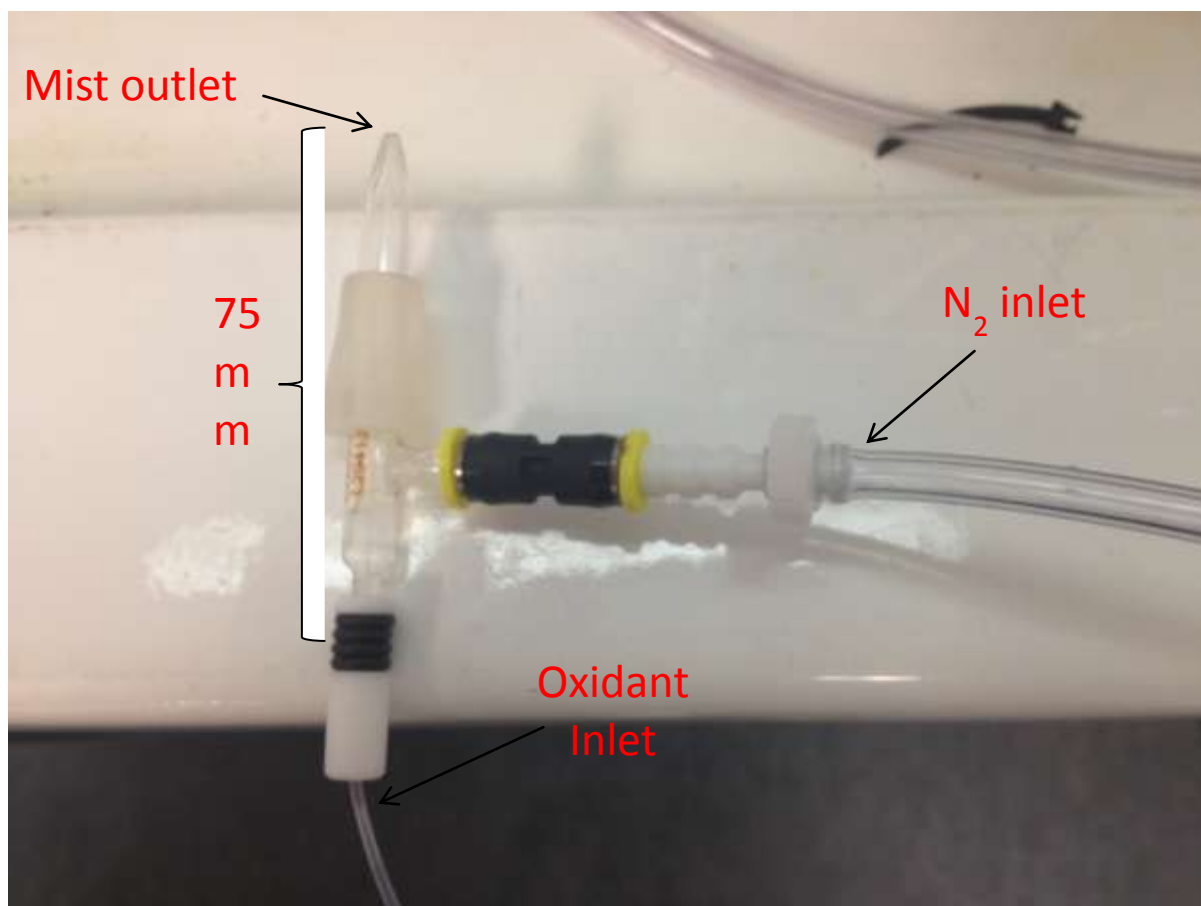


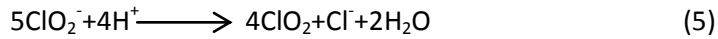
Figure.3. Nebulizer

The whole procedures can be described in a simple explanation. In fact, gas stream containing NO_x/N_2 was flowed into the spray chamber, therefore, gas flow rates can be varied during the experiment to meet mist production requirement. It is normally 1L/min based on nebulizer specification. Once mist was produced, it contacted with the toxic gas and oxidation-absorption process commenced. The idea by which mists were formed, was because of having huge surface area which caused quick and efficient oxidation-absorption process. In other words, small droplet were moving upward while contacting toxic gas could be influenced by inertial impaction, direct interception as well as Brownian diffusion[16]. This means that significant gas-liquid interfacial area was obtained, which resulted in low consumption of oxidant as well as low waste formation. Ultimately, each experiment took almost 15-20 min and majority of nitric oxides removal occurs in seconds since it is in the fast reaction regime. Nebulizer mists up the solution upward and oxidation-absorption occurred resulting in 100% -86% removal of NO and NO_x respectively. pH played a key role in this study, therefore, all experiments were carried out using buffers which caused the pH remained constant throughout the whole process. Boric acid, phosphate, sodium bicarbonate and acetic acid were used as buffers in the wet spraying medium. This study mainly encompasses the effect of various pH on nitric oxides removal.

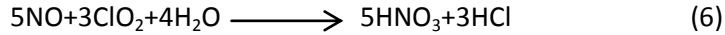
Results and discussion

Acidic medium

In acidic medium, where pH is low, chlorine dioxide (ClO_2) is formed. ClO_2 formation could be attributed to decomposition of NaClO_2 solution. Reaction (5) demonstrates ClO_2 formation [17].



ClO_2 is a strong oxidant that can react with NO and oxidise it to NO_2 , which is highly soluble in water. Reaction (6) shows how NO gets oxidised to NO_3^- by ClO_2 . One of the ways to detect chlorine dioxide is to check the colour of the solution. Once the colour turned to greenish-yellow, it can be confirmed that ClO_2 exists in the solution [6].



In order to find dominant reaction, pH value and chlorite concentration play a key role in oxidation-absorption process. In acidic medium oxidative ability of NaClO_2 solution is powerful and converts NO to NO_2 [17]. In our experiment, buffer solutions were used in order to keep the pH level constant [18]. Experiments were carried out in the range of $3 < \text{pH} < 7$ to check the NO_x removal. According to the experimental section, 470 ppm NO_x entered the spray chamber with 1L/min flow rate and contacted NaClO_2 solution at $\text{pH} = 4 \pm 0.2$, as a result, 72% of NO_x was removed. It should be noted that this removal procedure has also led to desorption of NO_2 from NaClO_2 solution. In other words, NO_2 increased and desorbed to gas phase owing to its saturation in liquid phase. This pH cannot be optimum since NO_2 level rose almost 5 times more than inlet which was 20 ppm. Fig.4. depicts that NO_2 increased; while, NO has reached zero. For this experiment, (sodium acetate, acetic acid) was used as a buffer solution. Another experiment was conducted at $\text{pH} = 6$ with phosphate buffer (Na_2HPO_4 , NaH_2PO_4) and the result was almost similar to that of $\text{pH} = 4$. In fact, 78% of NO_x removed; while, NO_2 concentration reached a high level, which is unacceptable. Powerful oxidative ability and poor absorption state could be the reason of low efficiency as well as high NO_2 desorption. Moreover, in acidic state there is no hydrolysis of N_2O_3 and N_2O_4 which result in absorption of NO_2 . Considering that this study investigates the optimum pH at which NO and NO_2 get removed, we must find a way to control ClO_2 formation. Acidic medium cannot be the solution; however, oxidation ability is high in acidic state. In other words, controlling of NO_2 formation along with ClO_2 was the agenda of this study. Since our experiments have been simulated as to they are in a condition in which a post-blast gases are present, acidic solution of NaClO_2 not only desorb NO_2 but also forms ClO_2 which is hazardous for the environment. Therefore, alkaline solution of NaClO_2 was employed to assist us removing NO_2 as well as ClO_2 to the best of its ability. Fig.6. obtained by FT-IR shows that a great amount of ClO_2 was formed during the experiment in acidic medium.

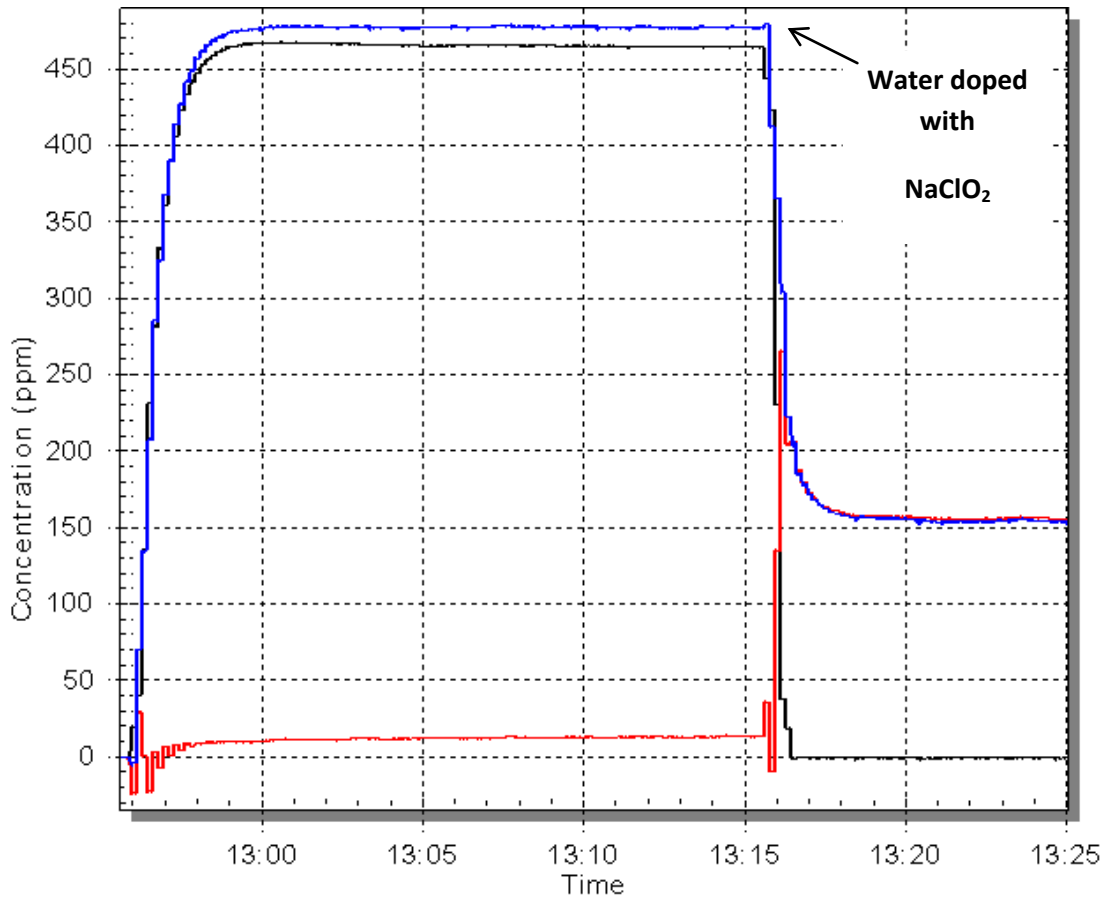


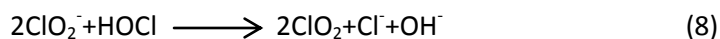
Figure.4. NO_x removal graph in acidic condition, pH<4

Alkaline medium

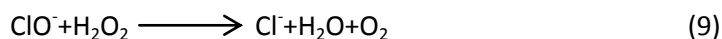
Having discussed NO removal using acidic solution of NaClO₂, alkaline medium should be considered. The beauty of alkaline reaction is when NO₂ reacts with chlorite and nitrate (NO₃⁻) is produced. The following reaction can be considered NO₂ reaction with ClO₂⁻.



Hydrolysis reaction of NO₂ plays a key role along with above reaction. As it was described earlier, ClO₂ formation should be avoided; however, there is no decomposition of NaClO₂ solution since it only occurs in acidic condition. It should be noted that hypochlorite was formed and reacted with chlorite ion to produce ClO₂, which is an undesirable product although it has powerful oxidative ability. Reaction (8) can be considered to be:



Hypochlorite ion (ClO⁻) is said to be produced at pH 7-10, however, it was not detected by chromatography due to low conductivity[12]. Reaction (8) occurs when pH drops below 10; therefore, buffer was used to keep pH constant over the course of the reaction. There is also an alternative to suppress ClO₂ formation which can be justified by the following reaction.



Reaction (9) is applicable for the reaction occurring when pH value drops below 7. Given the importance of mitigation of toxic gasses such as NO₂ and ClO₂ it was proven that alkaline solution

works much better than acidic solution with strong oxidative ability. Fig.5.1. shows how much NO_x is removed over the course of experiment. Fig.5.2. depicts that a very negligible amount of ClO₂ is formed once alkaline solution is applied. Whereas, Fig. 6. Shows how acidity can affect the process by producing huge amount of ClO₂.

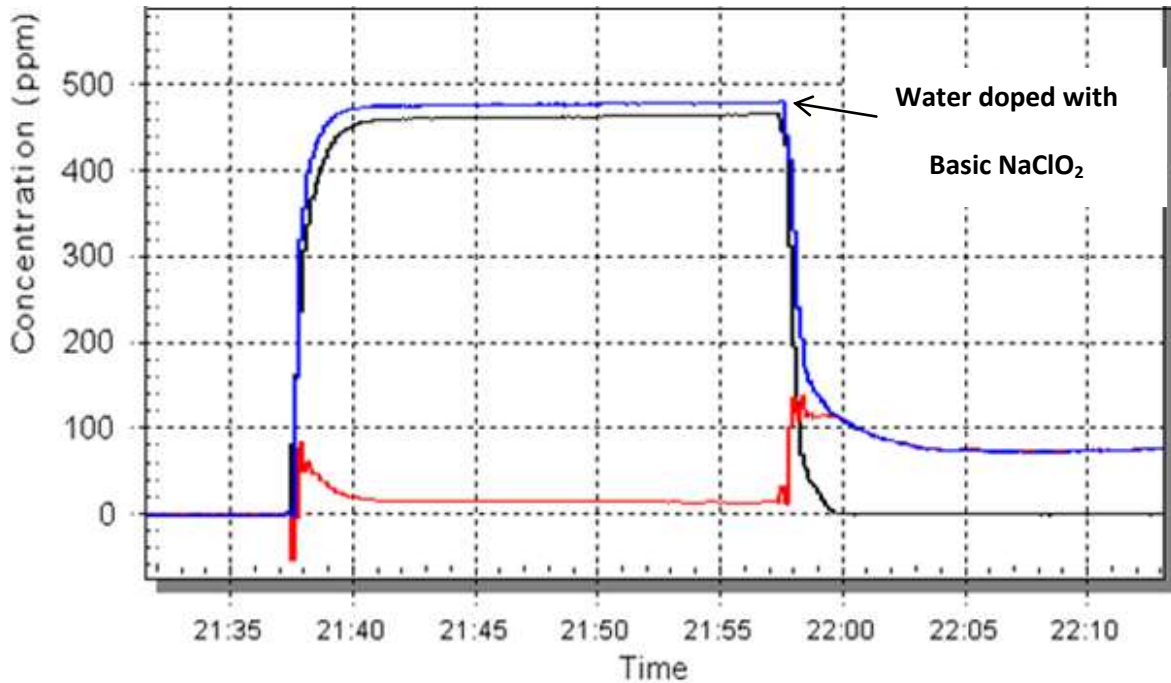


Figure.5.1. NO_x removal graph in acidic condition, pH>11

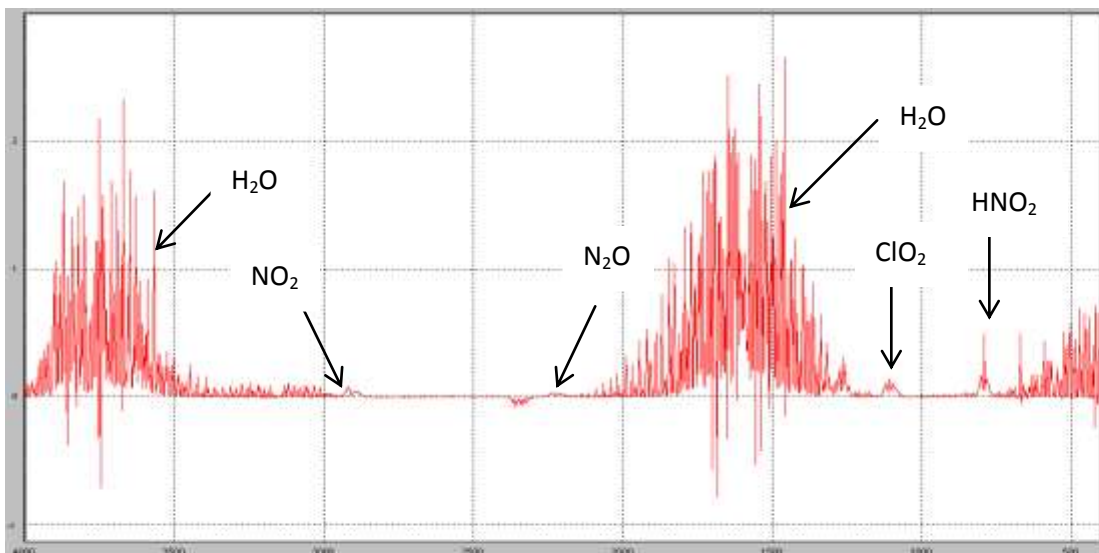


Figure.5.2 Spectra of gaseous at pH value>12 compounds obtained by FT-IR

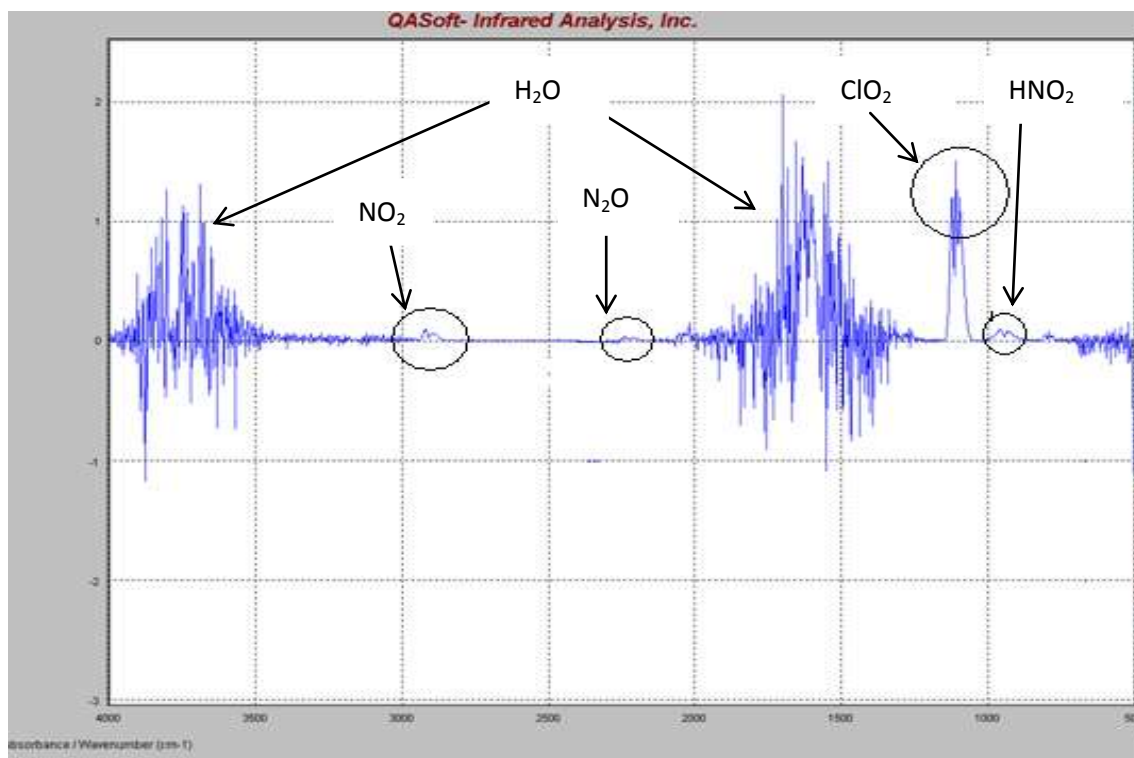


Figure.6. Spectra of gaseous at pH value<4 compounds obtained by FT-IR

Conclusions

Results of this study demonstrate that alkaline NaClO₂ solution has more advantages than acidic one. It showed that 100% removal of NO was observed with 86% NO_x removal containing NO₂, plus, a buffered solution of NaClO₂ demonstrated higher absorption and stability; moreover, a negligible amount of ClO₂ was formed when pH>11. Optimal NO and NO₂ absorption was found to be at pH value >11 due to having low concentration of ClO₂ in the gas phase.

Acknowledgment

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