Aqueous absorption of NOx induced by sodium chlorite oxidation

Chen-Lu Yang
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Aqueous Absorption of $\text{NO}_x$

Induced by Sodium Chlorite Oxidation

BY

Chen-Lu Yang

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Environmental Science. 1989
Title of thesis: Aqueous Absorption of NO$_x$ Induced by Sodium Chlorite Oxidation

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Master of Science in Environmental Science, 1989

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Professor of Chemical Engineering

Date approved: ____________________________

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Dr. Joseph W. Bozzelli Date

________________________________________
Dr. Richard Trattner Date
VITA

Name: Chen-Lu Yang

Degree and date to be conferred: M.S. in Environmental Science, 1989

Secondary education: Makong Provincial High School

College attended | Date | Degree | Date of degree
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NJIT | 87-89 | M.S. | 1989

Major: Environmental Science

Position held: Research Assistant of the Gas Scrubbing Laboratory at NJIT, Newark, N.J.
Aqueous scrubbing in alkaline media for the removal of nitrogen oxides (NO\textsubscript{x}) from flue gases using NaClO\textsubscript{2} as an oxidant is being investigated in the Chemical Engineering Department of New Jersey Institute of Technology. This thesis presents the findings of an experimental program that was conducted to estimate the capability of NaClO\textsubscript{2} aqueous solution to oxidize insoluble NO to soluble NO\textsubscript{2} in order to increase its solubility and thus prevent NO\textsubscript{x} emission from entering the atmosphere from flue gases emitted by municipal incinerators or power plants.

The key findings of this program are:

* NO is not absorbed by NaOH aqueous scrubbing solutions.
* NO\textsubscript{2} is essentially quantitatively absorbed in NaOH aqueous scrubbing solutions.
* Addition of NO\textsubscript{2} improves NO absorption in NaOH solution.
* NaClO\textsubscript{2} containing aqueous scrubbing medium quantitatively oxidizes NO to nitrate.
* Concentrations greater than 0.1M NaOH inhibit NO absorption in 0.008M NaClO₂ containing aqueous scrubbing media.

* Aqueous scrubbing media containing less than 0.1M NaOH quantitatively absorb NO induced by NaClO₂ oxidation.

* The presence of 5% Oxygen in flue gases reduces by 11.5% NO absorption induced by NaClO₂ oxidation.

* Mass transfer rather than chemical reaction kinetics seems to dominate the NO absorption process.
ACKNOWLEDGEMENT

The author is most grateful to his advisor, Dr. Henry Shaw, who has contributed in so many ways to make this research a great success.

My special thanks go to Dr. Joseph W. Bozzelli and Dr. Richard Trattner, for their thoughtful advice, helpful suggestions and ideas in conducting this research.

The author acknowledges with much appreciation the direct and indirect assistance by his colleague Joseph Chou.
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1. INTRODUCTION

Nitrogen oxides (NO$_x$) are mixtures of compounds of nitrogen and oxygen, namely, N$_2$O, NO, N$_2$O$_3$, NO$_2$, N$_2$O$_4$ and N$_2$O$_5$ generally found in effluents from combustion sources. The predominant NO$_x$ compounds are NO and NO$_2$. They are formed as a result of the reactions of atmospheric nitrogen with atmospheric oxygen at high temperatures. Also, large quantitative of NO$_x$ are formed from the oxidation of nitrogen compound found in fuel or in wastes being incinerated. More than 90% of NO$_x$ emitted from stationary combustion sources consist of NO which is relatively insoluble in inorganic aqueous solution. Finding a way to control NO is essential for the prevention of NO$_x$ pollution.

The molecular and thermodynamic properties of NO according to Yost and Russel (1944) are summarized in Table 1. Its bonding type can be studied by magnetic measurements, by which the participation of the odd electron in the bond is probed, or by measuring the change in the bond strength between nitrogen and oxygen atoms, as manifested by its infrared spectra. The configuration of NO molecular orbitals and the bonding of the nitric oxide group is illustrated in Figure 1 (M. Shelef 1971).

1-1 NO$_x$ formation and sources

Nitrogen oxides are emitted as nitric oxide (NO) from a variety of sources. The estimated emissions of NO$_x$ have large uncertainties associated with them. About 70-90% of Atmospheric
NO\textsubscript{x} emission are from anthropogenic sources in the world (Singh 1987).

Table 1 Molecular and Thermodynamic properties of NO

<table>
<thead>
<tr>
<th>Molecular Properties</th>
<th>Thermodynamic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy</td>
<td>m.p.</td>
</tr>
<tr>
<td>151 Kcal/Mole</td>
<td>109.49%</td>
</tr>
<tr>
<td>Bond length</td>
<td>ΔH fusion</td>
</tr>
<tr>
<td>1.15 Å</td>
<td>549.5 cal/mole</td>
</tr>
<tr>
<td>1st ionisation potential</td>
<td>b.p.</td>
</tr>
<tr>
<td>9.5 V</td>
<td>121.36%</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>ΔH vaporisation</td>
</tr>
<tr>
<td>0.16 Debye</td>
<td>3293 cal/mole</td>
</tr>
<tr>
<td>Molal susceptibility, 20°C</td>
<td>ΔH°f,298K</td>
</tr>
<tr>
<td>1.43×10^{-3} cgs units</td>
<td>ΔS°f,298K</td>
</tr>
<tr>
<td>Ground state</td>
<td>ΔG°f,298K</td>
</tr>
<tr>
<td>2\eta/2</td>
<td>+21,500 cal/mole</td>
</tr>
<tr>
<td>1st excited state</td>
<td>50.35 e.u.</td>
</tr>
<tr>
<td>2\eta/2</td>
<td>+20,650 cal/mole</td>
</tr>
<tr>
<td>ΔE(2\eta/2 - 2\eta/2)</td>
<td>352 cal/mole (124.2 cm\textsuperscript{-1})</td>
</tr>
</tbody>
</table>

Figure 1 Bonding and Electron configuration of NO

<table>
<thead>
<tr>
<th>Atomic Orbitals</th>
<th>Molecular Orbitals</th>
<th>Atomic Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>NO</td>
<td>O</td>
</tr>
<tr>
<td>2p\textsubscript{z} 2p\textsubscript{y} 2p\textsubscript{x}</td>
<td>\sigma^{+}2p\textsubscript{z}</td>
<td>2p\textsubscript{z} 2p\textsubscript{y} 2p\textsubscript{x}</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>\pi^{+}2p\textsubscript{y}</td>
<td>π\textsuperscript{+}2p\textsubscript{x}</td>
<td>π\textsuperscript{+}2p\textsubscript{x}</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>π 2p\textsubscript{y}</td>
<td>\pi 2p\textsubscript{x}</td>
<td>\pi 2p\textsubscript{x}</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>σ 2p\textsubscript{z}</td>
<td>σ 2p\textsubscript{z}</td>
<td>σ 2p\textsubscript{z}</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>σ 2p\textsubscript{z}</td>
<td>σ 2s</td>
<td>σ 2s</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>σ 2s</td>
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<td>σ 2s</td>
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<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>2s</td>
<td>2s</td>
<td>2s</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
</tbody>
</table>
1-1-1 Fossil fuel combustion and biomass burning

Thermally generated NO\textsubscript{x} results from the reactions of oxygen-nitrogen mixture exposed to a high temperature. The maximum concentration of NO\textsubscript{x} can be estimated from the equilibrium composition of an oxygen-nitrogen mixture as a function of temperature (Shelef, 1971). The equilibrium compositions of NO as a function of temperature are summarized in Table 2.

The key chemical reactions in the oxygen-nitrogen mixture at temperature below 4,500 K are given in Table 3. Dissociation of N\textsubscript{2} into atomic nitrogen becomes important above 4,500K (Seinfeld, 1986).

1-1-2 Lightning

The major natural source of NO\textsubscript{x} is caused by the effect of atmospheric lightning on atmosphere oxygen and nitrogen. The temperature of a column of air exposed to atmospheric lightning is a function of energy deposition of the lightning. For a typical energy deposition of about 10\textsuperscript{5} J/m, the column of air immediately surrounding the charge is heated to temperature on the order of 30,000K. At temperature above 2,300K, NO is in thermodynamic equilibrium with N\textsubscript{2} and O\textsubscript{2}. As the temperature of the heated air drops below 2,000K, NO "freezes" as a stable compound.

The total global production of NO due to atmospheric
Table 2: Equilibrium Concentration of NO in Nitrogen-Oxygen Mixture

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Equilibrium NO Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$1.549 \times 10^{13}$</td>
</tr>
<tr>
<td>400</td>
<td>$1.413 \times 10^{11}$</td>
</tr>
<tr>
<td>500</td>
<td>$6.223 \times 10^8$</td>
</tr>
<tr>
<td>600</td>
<td>$1.663 \times 10^7$</td>
</tr>
<tr>
<td>700</td>
<td>$1.268 \times 10^5$</td>
</tr>
<tr>
<td>800</td>
<td>$1.828 \times 10^3$</td>
</tr>
<tr>
<td>900</td>
<td>$4.046 \times 10^2$</td>
</tr>
<tr>
<td>1000</td>
<td>$1.208 \times 10^4$</td>
</tr>
<tr>
<td>1100</td>
<td>$4.508 \times 10^3$</td>
</tr>
<tr>
<td>1200</td>
<td>$1.977 \times 10^3$</td>
</tr>
<tr>
<td>1300</td>
<td>$9.863 \times 10^2$</td>
</tr>
<tr>
<td>1400</td>
<td>$5.433 \times 10^2$</td>
</tr>
<tr>
<td>1500</td>
<td>$3.236 \times 10^2$</td>
</tr>
<tr>
<td>1600</td>
<td>$2.056 \times 10^2$</td>
</tr>
<tr>
<td>1700</td>
<td>$1.380 \times 10^2$</td>
</tr>
<tr>
<td>1800</td>
<td>$9.683 \times 10^1$</td>
</tr>
<tr>
<td>1900</td>
<td>$7.047 \times 10^1$</td>
</tr>
<tr>
<td>2000</td>
<td>$5.297 \times 10^1$</td>
</tr>
</tbody>
</table>

Table 3: Key Reactions of Nitrogen-Oxygen Mixture at High Temperature

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Forward Reaction $\text{cm}^3\text{ molecule}^{-1}\text{sec}^{-1}$</th>
<th>Reverse Reaction $\text{cm}^3\text{ molecule}^{-1}\text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 + M \rightleftharpoons 20 + M^c$</td>
<td>$1.876 \times 10^{-6}T^{-1/2}\exp(-118,000/RT)$</td>
<td>$2.6 \times 10^{-33}$</td>
</tr>
<tr>
<td>$O + N_2 \rightleftharpoons NO + N$</td>
<td>$1.16 \times 10^{-16}\exp(-75,500/RT)$</td>
<td>$2.57 \times 10^{-11}$</td>
</tr>
<tr>
<td>$N + O_2 \rightleftharpoons NO + O$</td>
<td>$2.21 \times 10^{-14}T\exp(-7080/RT)$</td>
<td>$5.3 \times 10^{-15}T \times \exp(-39,100/RT)$</td>
</tr>
</tbody>
</table>
lightning is the product of two terms: 1) The yield of NO per energy input or lightning (J) or the NO per lightning flash and 2) the total energy deposited by lightning or the lightning flash frequency (Levine, 1984).

1-1-3 Microbial activity in soils

It has been found from field flux measurements and laboratory experiments that soil microrganisms may also produce appreciable amounts of NO. To quantify the rate of production of NO, a series of laboratory experiments were performed using two of the most common bacteria found in soils, Nitrosomonas Europaea and Alcaligenes Faecalis. The results indicate that nitrification is an aerobic process in which ammonium is oxidized to nitrite and nitrate. NO and N$_2$O are direct or indirect intermediates of this pathway (Levine, 1984).

1-1-4 Diffusion

NO$_x$ diffusion from the stratosphere is also an important source of tropospheric NO$_x$.

1-2 Health effects of NO$_x$

Little data exists on the health effects of NO$_x$ because exposure to these compounds is usually accompanied by concurrent exposure to other pollutants. Previous studies have demonstrated that NO$_2$ causes emphysema in several animal species.
EPA's "Cincinnati dog study" which used 0.64 ppm NO\textsubscript{2} in combination with 0.25 ppm NO, also indicated that the effect was progressive. The airway resistance of the lungs is known to increase when moderate exposures to NO\textsubscript{x} occurs. The principal epidemiological study of the effects NO\textsubscript{2} was conducted on the population of Chattanooga, Tennessee, in 1978, where manufacturing operations produced an atmosphere contaminated primarily by this compound. A conclusion from this study is that respiratory illness are higher than normal, if the concentration of NO\textsubscript{2} exceeds 0.06 ppm This study has been criticized for several reasons, but it remains the main source of data on the health effects of NO\textsubscript{2}.

1-3 Legislation

Man-made NO\textsubscript{x} emissions frequently accompany combustion. Various emission standards, limits and regulations have been promulgated to control NO\textsubscript{x} emission. In the USA, the primary standard for nitrogen dioxide is 100ug/m\textsuperscript{3}, taken as an annual arithmetic mean. But there is no standard for nitric oxide. Table 4 compare the emission standards of Sitzerland, Austria, Netherland, the FRG and Japan with the USA. The New Source Performance Standards for large utilities requires NO\textsubscript{x} emissions not to exceed 86g/EJ for gaseous fuels, 130g/EJ for liquid fuels and 260g/EJ for solid fuels (taken as NO\textsubscript{2}).
### Table 4. Emission Standards for New Power Plants

<table>
<thead>
<tr>
<th>State</th>
<th>Fuel (g MJ⁻¹)</th>
<th>State</th>
<th>Fuel (g MJ⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solid</td>
<td>liquid</td>
<td>gas</td>
</tr>
<tr>
<td>Switzerland</td>
<td>&gt; 300</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### 1-4 Technologies for NOₓ control

Emission of NOₓ has become a serious environmental problem and it is necessary for existing power plants plus municipal and industrial incinerators, utilizing high temperature processes, to remove the NOₓ from flue gases in order to comply with federal and local regulations.

In the past few years, a variety of processes have been proposed to eliminate this problem. These processes can be summarized as follows:

A). Combustion modification
* Low NO\textsubscript{x} burner design: Various burner designs have been proposed to lower the NO\textsubscript{x} emission such as tangentially fired boiler. Traditional cyclone burners produced high concentration of NO\textsubscript{x} in flue gas. Because the temperature of heat sinks of tangential firing burner almost equals to the temperature of burner flame, it reduces 50% to 60% thermal NO\textsubscript{x} formation (Maulbetsch, 1986).

* Flue gas recirculation: Flue gas recirculation is an effective method to reduce thermal NO\textsubscript{x}. The recirculated flue gas lowers the flame temperature and the oxygen contain in combustion. According to the report of EXXON research, 50% of flue gas recirculation reduces 60% thermal NO\textsubscript{x} formation (Sommerlad, 1971), (Shaw, 1981).

* Air-fuel staging in the combustion chamber: Thermal NO\textsubscript{x} formation can be reduced by operating the combustion in a fuel rich mode, followed by interstage cooling and burnout of the unburned compounds with excess air. Incomplete combustion in the first stage lowers thermal NO\textsubscript{x} formation. The second stage uses excess air to complete the combustion, reduce the combustion temperature and lower the thermal NO\textsubscript{x} formation (Bienstock, 1972). Alternatively, another method of interstage cooling can be used in order to
avoid a large excess of stoichiometric air.

B). Flue gas cleaning

* Selective noncatalytic reduction: NO\textsubscript{x} can be reduced to N\textsubscript{2} and H\textsubscript{2}O by introducing NH\textsubscript{3} into the effluent gas from a combustor at 930 to 990°C. The major disadvantages of this process are the narrow temperature window, the need for well mixed NH\textsubscript{3} and the possibility that NH\textsubscript{3} may break through (Seinfeld, 1988).

* Selective catalytic reduction: This process operates similarly to the thermal process except with a catalyst. The reactions occur at a much lower temperature of 300 to 400°C. There are commercial catalysts containing noble metals or vanadia/titania that can control NO\textsubscript{x} by 90% for the former, and 80% by the latter. Much research is currently being conducted for using Zeolites to control NO\textsubscript{x} with NH\textsubscript{3} (personal communication with Dr. Henry Shaw).

* Adsorption by solids: A number of activated carbon processes have been proposed to remove NO from flue gas. Copper oxide is also an effective adsorbent. Using these processes, Technologies of adsorbent regeneration and SO\textsubscript{2} removal are essential (Seinfeld, 1988).

* Wet process: In these processes, solvents are used to scrub NO from flue gases. chemical reaction is required
to adsorb NO in water. Those chemical reactions can be categorized to Gas Phase oxidation, liquid phase oxidation and, chelating reduction.

The gas scrubbing research presented here was conducted in the Gas Scrubbing Laboratory (room 206 Advanced Technology Center) of NJIT since May 1988. It is categorized as liquid phase oxidation, In this process, NO$_x$ is absorbed into alkaline solution and oxidized to nitrate.
2. GAS ABSORPTION

2-1 General concepts

Absorption is a diffusional process that involves the transfer of molecules from the gas phase into the liquid phase because of the concentration gradient between the two phases. The removal of contaminant by gas absorption occurs by bringing the gas into contact with a liquid in which the contaminant alone are soluble. Absorption of any species occurs at the surface of the liquid film (e.g., surrounding the packing (or mesh) or at the bubble surface when the gas is the dispersed phase).

Absorption is a unit operation that is enhanced by all the factors which normally affect mass transfer. There are high interfacial area, turbulent contact between the two phases, increased residence time, repetitive contact, high solubility, high diffusion coefficient, low liquid viscosity, and large negative Gibb's free energy changes in the case of reactive scrubbing. These factors influence the rate of mass transfer because they directly influence the concentration gradient.

The two film theory of gas absorption is the basic model of describing mass transfer from a gas to a liquid. The model is based on the theory that thin films exist on both sides of the phase boundary between gas and liquid. Molecular mass transfer or diffusion can only occur through these films. Figure 2 shows the interface behavior of two film theory for the complete range of
the reaction rate and mass transfer rate.

**Figure 2. Interface Behaviour of Two Film Theory**

![Diagram showing interface behaviour of two film theory with various reaction zones and phase interfaces.](image)
Case A, B, C and D: Reactions are so fast that component A is consumed before it diffuse into the main body of liquid. Reaction occurs only in the liquid film.

Case E and F: Reaction rates are intermediate with respect to mass transfer. Reaction will occur in both film and main body of the liquid.

Case G: Reaction rate is slow with respect to mass transfer. Reaction occurs in bulk liquid, however the film still provides a resistance of component A to transfer to the bulk liquid.

Case H: Reaction rate is infinitively slow with respect to mass transfer. Equilibrium is established and absorption is controled by chemical reaction only.

2-2 Physical absorption

The amount of a gas being physically absorbed in a liquid is determined by the solubility of the gas in the liquid. Solubility can be expressed in terms of partial pressure through Henry's Law as

\[ P_a = H_a \times X_a \]

Where \( H_a \): Henry's Law constant of A
\( P_a \): partial pressure of A
\( X_a \): mole fraction of A in liquid phase

The mass transfer rate is the product between the mass transfer coefficient and the concentration difference between the
bulk and the phase boundary.

\[ N_a = K_a (P_{ag} - P_{al}) \]

In this case we may lump Henry's Law constant into the relation between overall mass transfer coefficient, \( K_a \), gas phase mass transfer coefficient, \( K_{ag} \) and liquid phase mass transfer coefficient, \( K_{al} \)

\[ \frac{1}{K_a} = \frac{1}{K_{ag}} + \frac{H_a}{K_{al}} \]

Henry's Law is obeyed, when

1) The concentration of dissolved gas is very low.
2) The temperature and pressure are far away from the critical temperature and pressure of the gas, and
3) The gas does not change it's molecular structure when it dissolves (Bethea, 1978).

Physical absorption models are not suitable for reactive scrubbing process.

2-3 Chemical absorption

When a scrubbing solution contains a compound B, which can react with A, the contaminant in gas phase, it is refer as chemical absorption. The compound will prevent the concentration of A to build up in the bulk liquid. The overall rate expression for the reaction will have to account for the mass transfer
resistance (to bring reactants together) and the resistance of the chemical reaction step. Since the relative magnitude of these two resistances can vary greatly, we have a whole spectrum of possibilities, and since each situation requires its own analysis, our first problem is to identify these kinetic regimes and to select the one which matches the given physical situation.

Depending on the relative rates of diffusion and reaction the absorption systems are classified into five different regions (Levenspiel, 1972).

* Case A: Instantaneous reaction with respect to mass transfer. Consider an infinitely fast reaction of any order:

\[ aA \text{(from gas)} + bB \text{(liquid)} \rightarrow \text{product} \]

We have

\[
-r'_A = \frac{1}{S} \frac{dN_A}{dt} = \frac{b \frac{D_B}{D_A} C_B + \frac{p_A}{H_A}}{1 + \frac{1}{H_A k_{r_A}}} + \frac{1}{k_{Al}}
\]

If \( C_a \) is not too high, we have the situation shown in Figure 3.

* Case B: For fast second order reaction rate between A and B, the rate expression can be written as follows:

Where \( E = \frac{\sqrt{D_A} k_{C_A}}{k_{Al}} = \frac{\sqrt{D_A} k_1}{k_{Al}} \)
* Case C: Intermediate Rate with respect to mass transfer. These cases represent the general situation where reaction occurs both within thin film and within the main body of liquid. The general rate expressions for this regime have not been determined.

For our purposes, it suffice to note that the rate is
dependant on both interfacial surface and on volume of liquid, thus the ratio

\[ \frac{s}{v} \]

Where \( s \) is interfacial surface
\( v \) is the volume of liquid

becomes a parameter in this regime.

* Case D: Slow reaction with respect to mass transfer. Here the two films and main body of liquid act as resistances in series, thus we may combining and eliminating intermediate concentrations and produce the rate expression as follows (Levenspiel, 1972):

\[
\begin{align*}
-\frac{1}{S} \frac{dN_A}{dt} &= \frac{1}{\frac{H_A}{k_{A2}} + \frac{H_{A1}}{k_{A1}}} \rho_A \\
\frac{1}{V_1} \frac{dN_A}{dt} &= \frac{1}{\frac{H_A}{k_{A2}a_i} + \frac{H_{A1}}{k_{A1}a_i} + \frac{H_B}{k_{B}} \rho_A} \\
\text{gas} & \quad \text{liquid} & \quad \text{bulk} \\
\text{film} & \quad \text{film} & \quad \text{liquid}
\end{align*}
\]

* Case E: Infinitely slow reaction: Here the mass transfer resistance is negligible, the composition of A and B are uniform in the liquid, and the rate is determined by chemical kinetics only. The rate can be given directly by
Usually cases A and B describe gas scrubbing process for air pollution control.

2-4 Controlling factor determination

Absorption is classified into physical and chemical absorptions. Since there is no reaction in physical absorption, it is controlled by solubility while either chemical reaction or diffusion may control a chemical absorption.

2-4-1 Physical absorption controlling factor determination

The value of Henry's Law constant and the relation between the overall, gas phase and liquid phase mass transfer coefficients can be used to determine which phase controls the rate of mass transfer in a physical absorption process.

The gas phase resistance is controlling when the gas is highly soluble. This means that there is virtually no resistance in absorbing the gas once it reaches the liquid interface. A high solubility also implies a high diffusion rate in the liquid phase. Therefore the rate controlling step must either be gas
phase diffusion or the resistance associated with crossing the interface. Since the two film theory assume that there is no resistance at the interface, the gas phase diffusion is the controlling factor in this case.

The opposite situation occurs when one component has limited solubility in the liquid phase. There is resistance to dissolution. The diffusion in the liquid will be low. As the gas phase maintains a nearly saturated interface, the mass transfer rate depends on the rate at which the solute can be removed from the interface. In this case, the local and liquid film coefficients for mass transfer are approximately the same.

If the value of the Henry's law constant is < 0.187 atm. l/g.mole, the gas phase controls the rate of mass transfer. If H > 187.3 atm.l/g.mole, the liquid phase is controlling.

Another way to determine which phase offers the most resistance is to examine the ratio of the local and overall mass transfer coefficients. If \( K_g / K_{og} < 2 \), the gas phase probably controls. If this is < 1.1, the gas phase definitely controls. If the ratio is high, about 10, the liquid phase is controlling (Bethea, 1978).

As a general rule, gas phase diffusion is much faster than liquid phase diffusion and thus governs the type and size of the absorption equipment selected for any particular application.

2-4-2 Chemical absorption controlling factor determination
To determine whether a reaction is fast or slow, we focus on unit surface of gas-liquid interface. We assume that gas phase resistance is negligible and we define a film conversion parameter (Levenspiel, 1972):

\[ M = \frac{\text{maximum possible conversion in film}}{\text{maximum diffusion transport through film}} = \frac{kC_{A0}C_{B0}x_0}{x_0C_{A0}x_0} = \frac{kC_{B0}b_{Al}}{k_{Al}^2} \]

If \( M \gg 1 \) all reaction occurs in the film, and surface area is the rate controlling factor. On the other hand, if \( M \ll 1 \), no reaction occurs in the film, and bulk volume becomes the rate controlling factor. More precisely, it has been found that:

A) If \( M > 4 \), reaction occurs in the film and we have cases A and B in previous section.

B) If \( 0.0004 < M < 4 \), we then have the intermediate cases, C and D.

C) If \( M < 0.0004 \), we have the infinitely slow reaction of case E.

For process design, when \( M \) is large, a contacting device is chosen which develops or creates large interfacial area, energy for agitation is usually an important consideration. On
the other hand, If $M$ is very small, all we need is a large volume of liquid.
3 A LITERATURE REVIEW OF NO ABSORPTION

The removal of NO$_x$ from flue gases has received considerable attention due to federal regulations associated with the "Clean Air Act". The absorption of NO$_x$ from flue gases is very complex because:

a) The NO$_x$ gas is a mixture of several components consisting primarily of NO and NO$_2$ but could contain trace amounts of N$_2$O, N$_2$O$_3$, N$_2$O$_4$, and N$_2$O$_5$.

b) More than forty equilibrium reactions may be needed to explain the chemistry between nitrogen oxides and oxyacids.

c) Absorption and desorption operations occur simultaneously.

d) All kinds of complex reactions occur in this system.

e) Needed physical-chemical data is generally not available.

During the past fifty years, much data have been published in various aspects of NO$_x$ absorption. Much of these data were compiled in order to define areas for the future research.

3-1 Equilibrium

In the absorption of NO$_x$ gas in aqueous solutions, every component in the system takes part in one or more reaction with other components. Equilibria occur in the gas as well as in the liquid phase. In the following section, this type of information will be reviewed.

3-1-1 Gas phase equilibrium
The following equilibria occurs in the gas phase:

\[
\begin{align*}
K_1 & \quad 2 \text{NO}_2(g) \rightleftharpoons N_2\text{O}_4(g) \\
K_2 & \quad \text{NO}(g) + \text{NO}_2(g) \rightleftharpoons N_2\text{O}_3(g) \\
K_3 & \quad \text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2 \text{HNO}_2(g)
\end{align*}
\]

Where \(K_1, K_2\) and \(K_3\) are the pressure based equilibrium constants of each reaction. The \(K_1\) value is given by the following equation (Bronsted, 1922; JANAF 1971):

\[
\log K_1 = \frac{2993}{T} - 11.232
\]

In SI unit (kPa\(^{-1}\)) and \(T\) in K.

The \(K_2\) value is given by (Beattie, 1963; Beattie and Bell, 1947):

\[
\log K_2 = \frac{2072}{T} - 9.240 \quad \text{(kPa}\,^{-1})
\]

The value of \(K_3\) reported by Wayne and Yost (1951); Waldorf and Babb (1964); Ashmore and Tyler (1961) and Karavev (1962) is \(1.4 \times 10^{-2}\) at 25°C. However, the NBS (1968) and JANAF (1971) compilations give the values of 1.7 and 0.194 kPa\(^{-1}\) respectively. Schwartz and White (1981) analyzed the published literature and they compiled the data on standard free energies of formation summarized in Table 5.
### Table 5 Standard Free Energies and Enthalpies of Formation at 298 K

<table>
<thead>
<tr>
<th>Species</th>
<th>Standard Free Energy of Formation $\text{kJ/kmole} \times 10^{-3}$</th>
<th>Standard Enthalpy of Formation $\text{kJ/kmole} \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>51.32</td>
<td>33.19</td>
</tr>
<tr>
<td>NO</td>
<td>86.61</td>
<td>90.29</td>
</tr>
<tr>
<td>N$_2$O$_3$</td>
<td>139.48</td>
<td>83.76</td>
</tr>
<tr>
<td>N$_2$O$_4$</td>
<td>97.87</td>
<td>9.17</td>
</tr>
<tr>
<td>N$_2$O$_5$</td>
<td>115.12</td>
<td>11.30</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>-74.18</td>
<td>135.12</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>-46.05</td>
<td>-79.53</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>-228.70</td>
<td>-241.934</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>-237.292</td>
<td>-285.967</td>
</tr>
</tbody>
</table>

### 3-1-2 Aqueous phase equilibria

Aqueous phase equilibria can be written in terms of gas phase and mixed phase equilibria. Consider the following reactions:

$$2 \text{NO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{NO}_3^-(aq) + \text{H}^+(aq)$$

$$\text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O} \rightleftharpoons 2 \text{HNO}_2(aq)$$

$$2 \text{NO}(g) \rightleftharpoons 2 \text{NO}(aq)$$

These equations give:

$$3 \text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_3^-(aq) + 2 \text{NO}(aq) + \text{H}_2\text{O}(l)$$
Where \( K_{a1} = \frac{K_4}{(k_5)^2} \) \( H_{NO^2} \)

\[ 2 \ NO_2(1) \xrightarrow{K_{a2}} 2 \ H^+ + NO_2^- + NO_3^- \]

Where \( k_{a2} = \frac{K_4}{H_{NO^2}^2} \)

Schwartz and White (1981) reviewed the experimental data on liquid phase equilibrium. The result are summarized in Table 6. The symbol \( w \) in equations indicates that water take part in these reactions.

3-1-3 Solubility

(A) Nitric oxide (NO)

Solubility of nitric oxide in water with respect to temperature has been reported in International Critical Tables

Table 6 Aqueous phase equilibria

<table>
<thead>
<tr>
<th>No.</th>
<th>Equilibrium</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>( 3\ HNO_2(l) \ominus \ H^+ + NO_3^- + 2\ NO(l) )</td>
<td>( 1.12 \times 10^{-4} ) (kmole/m(^3))</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( 2\ H^+ + 3\ HNO_3 \lnot \ NO_3^- + 2\ NO(l) )</td>
<td>( 8.64 \times 10^{3} ) (kmole/m(^3))(^{-1})</td>
</tr>
<tr>
<td>( A_3 )</td>
<td>( 2\ NO_2(l) \lnot \ N_2O_4(l) )</td>
<td>( 6.54 \times 10^{4} ) (kmole/m(^3))(^{-1})</td>
</tr>
<tr>
<td>( A_4 )</td>
<td>( \text{NO}(l) + \text{NO}_2(l) \lnot \ N_2O_3(l) )</td>
<td>( 1.37 \times 10^{4} ) (kmole/m(^3))(^{-1})</td>
</tr>
<tr>
<td>( A_5 )</td>
<td>( 2\ NO_2(l) \lnot \ HNO_2(l) + H^+ + NO_3^- )</td>
<td>( 3.8 \times 10^{6} ) kmole/m(^3)</td>
</tr>
<tr>
<td>( A_6 )</td>
<td>( \text{N}_2\text{O}_3(l) \lnot \ 2\ HNO_2(l) )</td>
<td>( 3.3 \times 10^2 ) kmole/m(^3)</td>
</tr>
<tr>
<td>( A_7 )</td>
<td>( \text{NO}(l) + \text{NO}_3(l) \lnot \ 2\ HNO_2(l) )</td>
<td>( 4.52 \times 10^{6} ) —</td>
</tr>
</tbody>
</table>

*The symbol \( \lnot \) indicates that water takes part in the reaction.*
(1928), Handbook of Chemistry and Physics (1963) and by Seidell and Linke (1965). The value of Henry's law constant can be correlated by the following equation

$$\log H_{\text{NO}} = \frac{-1463.32}{T} + 2.178$$

Where $H_{\text{NO}}$ is in kg mole/m$^3$ atm.

Armor (1974) has measured the solubility of NO as a function of pH (2-13). He has shown that, in the pH range studied, there was no change in the value of the solubility.

The solubility of NO in aqueous electrolyte solutions can be calculated by using the following equation

$$\log \left( \frac{H}{H_w} \right) = -\sum K_s * I$$

Where $H$ and $H_w$ are the values of solubility in the solution and water, respectively. $K_s$ is the salting out parameter and is given by the following equation

$$K_s = i^+ + i^- + i_g$$

Where $i^+$, $i^-$ are the contributions of the cations and anions of the electrolyte and $i_g$ is the contribution of the solute gas. Danckwerts (1970) reported the values of $i^+$ and $i^-$ for various cations and anions. On the basis of these values and the solubility data reported by Armor (1974) the value of $i_g$
for NO is 0.037 m³/k ion.

(B) Nitrogen dioxide (NO₂)

The determination of solubility of NO₂ in water is difficult because NO₂ reacts with water. Andrew and Hanson (1961) and Komigama and Inoue (1980) found the solubility of NO₂ in water using the theory of absorption followed by pseudo nth order chemical reaction. The value of Henry's law constant was found to be 0.04 at 25°C [Andrew and Hanson] and 0.024 at 15°C [Komiyama and Inoue]. This method needs the knowledge of diffusivity (D) of NO₂ in water and the reaction rate constant (k) between dissolved NO₂ and water.

Garcia et al., (1975) obtained a preliminary estimate of Henry's law constant of NO₂ on the basis of following equation

\[
\frac{H_{NO_2}}{H_{NO}} = \frac{H_{CO_2}}{H_{CO}}
\]

The value \(H_{NO_2}\) works out to be 0.07 (kgmole/ m³ atm) at 25°C. Schwartz and White (1981) have correlated the solubilities of gases with their boiling points. Using this relation the value of \(H_{NO_2} = 0.02\) was estimated at 25°C.

3-2 Absorption of NO followed by oxidation

Oxidation of NO is the most important step in the NO scrubbing process. Oxidation of NO to NO₂ is relatively slow, and thus, becomes the rate limiting step in most approaches. Further
more, chemical oxidation of NO is required when its concentration is very small. The common agents include; nitric acid, ozone, hydrogen peroxide, chlorine dioxide, chlorite, etc.

(A) Ozone

The reaction of NO with ozone is given by the following equation

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

The resulting nitrogen dioxide can conveniently be scrubbed in caustic solutions even at low ppm values. The mechanism of above reaction has been studied by Harcourt (1972) and Bhatia and Hall (1980). The kinetics has been investigated by Borders (1982).

(B) Sulfuric acid

Topol, et al., (1968) used sulfuric acid as the oxidizing agent. The reaction is represents by:

\[ 4 \text{NO} + 3 \text{H}_2\text{SO}_4 \rightarrow 2 \text{NO}^+ + 2 \text{NO}_2 + \text{H}_3\text{O}^+ + 3 \text{HSO}_4^- \]

\[ 2 \text{NO} + 5 \text{H}_2\text{SO}_4 \rightarrow 2 \text{NO}^+ + \text{SO}_2 + 2 \text{H}_3\text{O}^+ + 4 \text{HSO}_4^- \]

The equilibrium constant values of the first and second reactions were found to be \(2 \times 10^{50} \text{ (kgmole/m}^3)\) and \(4 \times 10^{12} \text{ (kgmole/m}^3)\), respectively. The rate of the second reaction was second order in NO and the rate constant was found to be 0.2 \(\text{m}^3/\text{kgmole s})\).

(C) Hydrogen peroxide
Takahashi et al., (1979) carried out gas phase NO oxidation using hydrogen peroxide. Nitric oxide and hydrogen peroxide were taken in the ratio of 1 : 13 at a temperature more than 400° C and using 100 ppm NO. The extent of NO oxidation was greater than 95%. Absorption experiments were carried out using 101.5 mm ID stirred cell by Lodhabhoy and Sharma (1969). The reaction between NO and H₂O₂ is given by the following equation

\[ \text{NO} + \text{H}_2\text{O}_2 \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O} \]

Absorption of NO is accompanied by fast pseudo first order chemical reaction. The value of reaction rate constant at 30 °C was found to be \(8.42 \times 10^2\) \((\text{m}^3/\text{kgmole s})\) with an activation energy of 13,700 kcal/kg mole.

(D) Potassium permanganate

Potassium permanganate was used for the oxidation of NO by Kann et al., (1976). Conversion of NO exceeding 80% has been reported. Sada et al., (1977) studied the oxidation of NO using aqueous solutions of KMnO₄ and aqueous solutions mixed solutions of KMnO₄ and NaOH.

In the absence of NaOH the reaction between NO and KMnO₄ can be represented by the following equation:

\[ \text{NO} + \text{MnO}_4^- \rightarrow \text{NO}_3^- + \text{MnO}_2(s) \]

Uchida et al., (1983) showed that the product of reaction with MnO₂ has some inhibiting effect on the rate of reaction.
In the presence of NaOH, the oxidation reaction enhances the reaction between NO and KMnO$_4$ in a strong aqueous caustic solution is given by

$$\text{NO} + \text{MnO}_4^- + 2 \text{OH}^- \rightarrow \text{NO}_2^- + \text{MnO}_4^{2-} + \text{H}_2\text{O}$$

Similar observation has been reported by Teramoto et al., (1969).

(E) Sodium chlorite

The absorption of NO in aqueous mixed solutions of NaClO$_2$ and NaOH has been studied by Teramoto et al., (1976) and Sada et al., (1978, 1979). Oxidation of NO with NaClO$_2$ in the presence of NaOH can be presented by

$$4 \text{NO} + 3 \text{ClO}_2^- + 4 \text{OH}^- \rightarrow 4 \text{NO}_3^- + 3 \text{Cl}^- + 2 \text{H}_2\text{O}$$

The rate constant decreases with an increase in the concentration of NaOH.

(F) Chlorine dioxide

Two Japanese patents claim the use of chlorine dioxide for NO oxidation (Kushiro, et al., 1976 and Hayashi et al., 1976) The process was applied the removal of NO from flue gas. The conversion with respect to NO has been claimed to be about 90%.

(G) Sodium sulfite

Takeuchi, et al., (1977a, 1977b, 1978) have studied the absorption of NO in aqueous solutions of sodium sulfite at 25°C. The absorption of NO in Na$_2$SO$_3$ solution was accompanied by a fast pseudo second order reaction with respect to NO and zero
order in sulfite.

Uchida, et al., (1983) studied NO absorption which initially increases with \( \text{Na}_2\text{SO}_3 \) concentration, attains a maxima when \([\text{Na}_2\text{SO}_3]\) is 0.1 k mole/m\(^3\) and then decreases.

(H) Sodium dithionite

Lahari (1981) measured specific rates of absorption of NO in aqueous caustic solutions of sodium dithionite (\( \text{Na}_2\text{S}_2\text{O}_4 \)) and sodium sulfide (\( \text{Na}_2\text{S} \)) at 31°C and 27°C respectively. The reaction between NO and aqueous caustic solution of \( \text{Na}_2\text{S}_2\text{O}_4 \) was found to be first order with respect to NO only. The first order rate constant was found to be \( 2.3 \times 10^3 \) s\(^{-1}\) at 31°C. The reaction between NO and the caustic aqueous solution of sodium sulfide was found to be zero order in \( \text{Na}_2\text{S} \) and zero order in NO. The rate constant was found to be \( 1.69 \times 10^{-4} \) kgmole/m\(^3\) s at 27°C.

3-3 Absorption of NO followed by complex reaction

(A) FeSO\(_4\)

Kustin, et al., (1966) have reported that the NO absorption into FeSO\(_4\) solution is an equilibrium reaction

\[
\text{NO} + \text{FeSO}_4 <----> \text{Fe(NO)SO}_4
\]

The forward reaction was found to be first order in both NO and FeSO\(_4\). The reverse reaction was found to be first order with respect to the complex Fe(NO)SO\(_4\). Similar observations have been reported by Hikita, et al., (1977). The value of second order
rate constant for the forward reaction was given by the following equation:

\[
\log (k_2)_{\text{NO}} = 10.303 + 0.124 \ I - \frac{1337}{T}
\]

Where I is the ionic strength.

(B) Fe$^{3-}$-EDTA

The absorption of NO in aqueous solution of Fe$^{3-}$-EDTA and aqueous slurries of MgSO$_3$ with Fe$^{2-}$-EDTA was carried out by Sada, et al., (1981). The the forward complexing reaction was represented by:

\[
\text{NO} + \text{Fe}^{3-}\text{-EDTA} \rightarrow \text{Fe}^{3-}(\text{NO})(\text{EDTA})
\]

The reaction was found to be first order in NO and 1.5 order in Fe$^{3-}$-EDTA at pH of 7.0.

(C) Na$_2$SO$_3$/Fe$^{3-}$-EDTA-Na

Hikita, et al., (1978) performed a series of experiments for the NO absorption into Na$_2$SO$_3$/Fe$^{3-}$-EDTA-Na solution. The rate constants are independent of Na$_2$SO$_3$ concentration and dependent on Fe$^{3-}$-EDTA-Na, ionic strength of present and the temperature.

(D) Ferrous cysteine

The absorption of NO in Ferrous cysteine aqueous solution was reported by Shih-Ger Chang et al., (1988). The advantage over the conventional Fe$^{+2}$-EDTA system is cysteine can be regenerated. The best regeneration result were obtained from the reaction of CYS-CYS with H$_2$S and SO$_2$ at pH of 10.0 and 60$^\circ$C.
4 EXPERIMENTAL PROGRAM

The laboratory apparatus, chemicals and gases used to conduct the experimental program of this thesis are described in this section.

4-1 Apparatus

The basic scrubbing apparatus consists of a flue gas blending system, a matched pair of gas scrubbers and an analytical train. The blending system is capable of producing a mixture of nitrogen, oxygen, nitric oxide and nitrogen dioxide in order to simulate a wide variety of flue gas compositions by mixing pure gases components and blends in different proportions. The synthetic flue gas was introduced into the scrubber through a polyethylene sparger. The effluent gases were carried to the gas analyzers for the determination of residual NO, NO₂ and O₂. The scrubber consists of a 5.1 cm diameter by 61 cm long pyrex pipe capped on both ends with 0.63 cm entrance and exit polyethylene tubes. The components of the scrubbing system are described in detail below.

4-1-1 Flue gas blending system

The flue gas blending system is designed to provide synthetic flue gas from high pressure gas cylinders. The blending system is constructed out of 0.63 cm diameter (O.D.) by 60 cm long stainless steel type 316 tubing. Each component gas is
delivered through a 0.32 cm (O.D.) teflon tubing to a calibrated rotameter to the blending manifold. The total flow rate from the blending system ranged from 8.9 to 0.4 standard liters per minute. Figure 4 presents the schematic of the gas blending system.

4-1-2 Scrubbing vessels

The flue gas scrubbers are 5.1 cm in diameter by 61 cm long Pyrex glass columns with a polyethylene sparger located at the bottom. The flue gas was introduced into the scrubbing solution through the sparger. Figure 5 contains a schematic of the scrubber design. Two scrubbing units are available, Either one could be used as the main scrubber while the other would be the reference scrubber.

One liter of scrubbing solution is generally used to run these experiments as semibatch process with continuous (1 l/min) flue gas injection. The actual scrubbing volume was varied as the flow rate in a few experiments. The exiting gas was carried to an oxygen monitor and NOx analyzer from the top of the glass column by 0.32 cm polyethelene tubing after removal of moisture. Liquid samples were removed periodically through a valve at the bottom of the glass column to measure solution pH. The same solution was then injected in a Dionex Ion chromatograph to measure the anion concentrations of reactant (ClO2⁻) and products (Cl⁻ and NO3⁻).
Figure 4 Schematic of the Gas Blending System

Figure 5 Schematic of Scrubber Design
When conducting a scrubbing experiment, the following sequence was followed:

* Set the flue gas composition and flow rate while flowing through the reference scrubber.
* Switch flue gas through the main scrubber (prefilled with the desire solution).
* Monitor pH and temperature.
* Check inlet flue gas composition using the oxygen monitor and NO\textsubscript{x} analyzer.
* Measure outlet composition as a function of run time.
* Take liquid sample periodically.
* Run liquid sample in ion chromatography.

4-2 Reagents

NaClO\textsubscript{2} and NaOH were used as the NO oxidizer and NO\textsubscript{2} neutralizer in the scrubber. The synthetic flue gas was produced by mixing NO, NO\textsubscript{2} and O\textsubscript{2} gases from high pressure gas cylinders with nitrogen making up the balance. The source and purity of these chemicals are discussed below.

4-2-1 Sodium chlorite

Commercial sodium chlorite containing approximately 80% NaClO\textsubscript{2}, 18% Na\textsubscript{2}CO\textsubscript{3} and 2% Na\textsubscript{2}SO\textsubscript{4} was supplied by Pfaltz & Bauer inc. Waterburg, CT 06708.

Textone is the commercial name of sodium chlorite, which is
prepared by the reaction of a reducing agent on chlorine dioxide in an alkaline medium.

Sodium chlorite is the sodium salt of the unstable chlorous acid, having a dissociation constant of $K_a = 0.01$. The salt exists both in anhydrous and a trihydrated form. The crystals of NaClO$_2$ are white, but they usually have a greenish tint because traces of chlorine dioxide are present. The chlorite anion is more stable than hypochlorite anion, but less stable than chlorate anion. In cold alkaline solutions, sodium chlorite has only mild oxidizing power. However, heating or acidification, or both, make chlorite solutions strongly oxidizing. Due to the strong oxidizing risk, sodium chlorite should never be stored in open containers.

4-2-2 Sodium hydroxide

Commercial sodium hydroxide (caustic soda, sodium hydride, lye, white caustic) NaOH was supplied by Pfaltz & Bauer, Inc. CT. 06708. It is a white deliquescent solid, absorbs water and carbon dioxide from the air. Its melting point is 318°C, boiling point is 1390°C. At normal condition, it dissolves in water, alcohol, and glycerol.

Sodium hydroxide is corrosive to tissue in presence of moisture: strong irritant to tissue (eyes, skin, mucous membranes). Its tolerance amount is 2 mg per cubic meter of air.

4-2-3 Gases
A) Nitric Oxide:

The nitric oxide was supplied as a 10% blend by Union Carbide Corporation
Linde Division
National Specialty Gases Office
100 Davidson avenue
Somerset, NJ 08873

By the following order informations and specifications
Cylinder type: T
Grade: custom blend
Concentration: 10% NO in nitrogen
Volume: 6.79 m³
Cylinder pressure: 14,824 kpa.
Regulator used: UPG-CGA 160/660 in stainless steel

Nitric oxide is a colorless gas, which is slightly soluble in water and noncombustible. It usually used to prepare nitrosyl carbonyl.

It is highly toxic by inhalation; strong irritant to skin and mucous membranes; supports combustion. Its tolerance concentration is 25 ppm in air.

B) Nitrogen Dioxide:

The nitrogen dioxide mixed cylinder was supplied as a 0.5% blend by Union carbide corporation, Linde Division. by the following order informations and specifications:

Cylinder type: T
Grade: custom blend
Concentration: 0.5% NO$_2$ in Nitrogen.
Volume: 6.79 m$^3$
Cylinder pressure: 14,824 kpa
Regulator used: UPG-CGA 160/660, stainless steel

Nitrogen dioxide is a red-brown gas or yellow liquid; becomes colorless solid at -11.2°C, which exists in varying equilibrium with other oxides of nitrogen as the temperature is varied.

Nitrogen dioxide is used in the production of nitric acid, nitrating agent, oxidizing agent, catalyst, oxidizer for rocket fuel, and polymerization inhibitor for acrylates.

NO$_2$ has been found to be very toxic, inhalation may be fatal. Its tolerance concentration is 5 ppm.

C) Oxygen:

The pure oxygen cylinder was supplied by Union Carbide Corporation, Linde Division by the following order informations and specifications

Cylinder type: T.
Grade: extra dry.
Minimum purity: 99.6%
Maximum moisture 10 ppm
Volume: 7.05 m$^3$
Weight: 69.5 kg
Cylinder pressure: 15,168 kpa
Regulator used: UPE-CGA 540 brass
Oxygen is a colorless, odorless, tasteless diatomic gas. It is actually a noncombustion gas, but actively supports combustion and may explode on contact with heat oxidizable material. High concentration oxygen also irritant to skin and tissue.

D) Nitrogen:

The nitrogen gas cylinder was supplied by Union Carbide Corporation, Linde Division. by the following order informations and specifications

Cylinder type: T
Grade: prepurified
Minimum purity: 99.998%
\( \text{H}_2\text{O} < 3 \text{ ppm} \)
\( \text{O}_2 < 5 \text{ ppm} \)
volume: 6.46 m\(^3\)
Weight: 67.7 kg
Cylinder pressure: 15,168 kpa
Regulator used: UPE-CGA 580 brass

Nitrogen is a colorless, tasteless diatomic gas constituting about four fifths of the air. The gas is noncombustible and slightly soluble in water and alcohol.

4-3 Analysis

Concentration changes were obtained by a train of analytical instruments. They are
* Chemiluminescent NO/NO\textsubscript{X} analyzer
  Model 10 A
  Thermoelectron Instruments Inc.

* Beckman NO/NO\textsubscript{X} analyzer
  Model 955
  Beckman Industrial Corp.

* Process oxygen monitor
  Model 715
  Beckman Industrial Corp.

* Beckman oxygen monitor
  Model 7005
  Beckman Industrial Corp.

* pH meter
  Model 6071
  Jenco Electronic LTD.

* Ion chromatography
  System 2120i
  Dionex Corporation

4-3-1 Flue gas analysis

The outlet line carrying the scrubber effluent entered a junction from which two lines exited. These lines deliver the effluent to the analyzers for measurement of the concentrations of NO, NO\textsubscript{2} and O\textsubscript{2}.

The Thermoelectron NO\textsubscript{X} analyzer is used to measure the
concentration of NO and NO₂. This instrument make use of the chemiluminescent properties of the NO reaction with ozone as a measure of NO concentration. NO molecules are mixed with O₃ from the ozone generator and carried into a reaction chamber where NO is electronically converted to excited NO₂. Excited NO₂ than emit light (Chemiluminescence).

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2
\]

\[
\text{NO}_2^* \rightarrow \text{NO}_2 + \text{hv}
\]

The basic chemiluminescent analyzer is only sensitive to NO molecules. NO₂ is measured by thermally converting the NO₂ to NO and measuring the incremental increase in concentration of NO. A temperature controller is used to maintain the proper temperature for NO₂ reduction. The proper temperature is 650°C.

Both concentrations of NO and NO₂ were analyzed by a Beckman 955 NO/NOx analyzer independently to double check the results.

Both instruments were calibrated with a analyzed mixture of 100 ppm NO and 109 ppm NO₂ in nitrogen. In all runs, the agreement between both measurements are better than 10%. The output signal from both analyzers were continuously recorded.

The oxygen concentration is determined with a Beckman model 715 process oxygen monitor. This instrument has an amperometric oxygen sensor, which contains a metallic cathode and anode. The two electrodes are separately mounted within the polypropylene body and are electrically connected by a potassium chloride
electrolyte. A constant potential is impressed across the two electrodes.

A gas-permeable teflon membrane separates the electrodes from the process sample and fits firmly against the cathode. Oxygen from the sample diffuses through the membrane and is reduced at the cathode. The resultant electrical current flow between the anode and cathode is proportional to the partial pressure of oxygen in the sample.

The sensor is calibrated with an analyzed 5% oxygen in nitrogen mixture and an air sample assumed to be 21% oxygen. Signal from the monitor is recorded continuously.

A Beckman model 7005 oxygen monitor is used to double check the result from model 715. The agreement between these two instruments is always better than 10%.

4-3-2 Scrubbing solution analysis

A Jenco 6071 pH meter was used to measure the pH value and temperature of the scrubbing solution. Janco 6071 is a microcomputer based pH/mv/temperature meter with following specifications:

* Range
  
pH: -2.00 to 16.00
  
Temperature: 0 to 100°C

mV: -999 to 999

* Resolution
pH: 0.01
Temperature: 0.1
mV: 1.0

* Accuracy
pH: 0.1%
Temperature: 0.5%
mV: 0.1%

Liquid samples were taken from the scrubber at regular time interval. Ionic concentrations were determined both qualitatively and quantitatively using Dionex ion chromatography system 2120i under the following conditions:

Column: BIO-RAD
IC-anion-PW
Catalogue-127-0062
Serio # 10825
Flow rate: 1.2 ml/min
Low pressure limit: 0 psi
High pressure limit: 700 psi
Temperature compensation: 1.7
Output range: 30 us

The sample injection is pushed by buffer eluent through the analytical column, where ions are separated. After separation, the sample is carried to a conductivity detector, which is based upon the electrical conductivity of the sample when placed between two oppositely charge electrodes. The presence of ions in
the solution allows electrical current to flow between the electrodes, completing the circuit. At low concentrations, conductivity is directly proportional to the concentration of conductive species in the solution. The total ionic concentration of the solution in the cell and the temperature of that solution affect the linearity of this relationship.

Table 7 contains data on a series of standard at varies concentrations. Figure 6 is the peak area-concentration calibration curve of Cl\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−}, using this curve, concentrations of Cl\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} can be obtained.
Table 7 Peak Area-Concentration Data of Cl\(^{-}\) and NO\(_3\)\(^{-}\) of Dionex IC System 2120i

<table>
<thead>
<tr>
<th>conc. ppm.</th>
<th>species</th>
<th>peak area (10^7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>Cl(^{-})</td>
<td>26.52</td>
</tr>
<tr>
<td></td>
<td>NO(_3)(^{-})</td>
<td>14.65</td>
</tr>
<tr>
<td>200</td>
<td>Cl(^{-})</td>
<td>15.05</td>
</tr>
<tr>
<td></td>
<td>NO(_3)(^{-})</td>
<td>7.08</td>
</tr>
<tr>
<td>100</td>
<td>Cl(^{-})</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td>NO(_3)(^{-})</td>
<td>3.52</td>
</tr>
<tr>
<td>50</td>
<td>Cl(^{-})</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td>NO(_3)(^{-})</td>
<td>1.61</td>
</tr>
<tr>
<td>25</td>
<td>Cl(^{-})</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>NO(_3)(^{-})</td>
<td>0.80</td>
</tr>
<tr>
<td>12.5</td>
<td>Cl(^{-})</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>NO(_3)(^{-})</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Figure 6 Relationship Between Peak Area and Concentration of Cl\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} of Dionex IC System 2120i
5 RESULTS

An aqueous scrubbing program was conducted to test sodium chlorite as an in situ oxidizer to absorb NO by means of oxidation and absorption in an alkaline solution from a gas stream that simulates the composition of incineration emission.

The objective of the scrubbing tests were to:
* Determine the potential of NaClO$_2$ aqueous scrubbing for NO oxidation and absorption.
* Obtain the rate parameters for NO oxidation to NO$_2$ by NaClO$_2$.

Experiments are detailed in the following sections.
5-1 Absorption of NO in Caustic Aqueous Scrubbing

A series of runs of aqueous scrubbing of flue gas containing NO of 300, 500, and 800 ppm in N₂ had been performed at following conditions

Flue gas:
- NO: 300, 500, 800 ppm
- Balance: N₂
- Flow rate: 1 l/min

Scrubbing solutions:
- NaOH: 0, 0.0001, 0.01, 1.0 M
- Volume: 1 liter

All tests were conducted at room temperature (25°C) and atmospheric pressure.

Results contained in Table 8 indicate that NO can not be absorbed by distilled water. Similarly, the presence of NaOH up to 1.0 M did not improve the NO absorption.
Table 8 Absorption of NO in Caustic Aqueous Scrubbing

<table>
<thead>
<tr>
<th>NO (ppm)</th>
<th>Expt</th>
<th>absorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conc. of NaOH (molarity)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>#</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>1.3</td>
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<tr>
<td>3</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>avg</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>avg</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>avg</td>
<td>0.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Absorption % = 1 - \( \frac{\text{NO (out)}}{\text{NO (in)}} \) * 100%
5-2 Absorption of NO\textsubscript{2} in Caustic Aqueous Scrubbing

A number of experiments were carried out to test the absorption of NO\textsubscript{2} in caustic aqueous scrubbing, which were conducted at the following conditions

Flue gas:
- NO\textsubscript{2}: 300, 500, 800 ppm
- Balance: N\textsubscript{2}
- Flow rate: 1 l/min

Scrubbing solutions:
- NaOH: 0.01, 0.1, 0.5 M
- Volume: 1 liter

The experiments were conducted at room temperature and pressure.

Data in Table 9 show that NO\textsubscript{2} can be effectively absorbed by NaOH solution. Runs with 0.5 M NaOH indicated that absorption of more than 98% is achieved.
Table 9 Absorption of NO\textsubscript{2} in Caustic Aqueous Scrubbing

<table>
<thead>
<tr>
<th>NO\textsubscript{2} (ppm)</th>
<th>Expt</th>
<th>absorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conc. of NaOH (molarity)</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>74.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>73.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>72.8</td>
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<tr>
<td></td>
<td>avg</td>
<td>73.4</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>80.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>80.3</td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>83.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>81.4</td>
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<td>3</td>
<td>80.6</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>81.8</td>
</tr>
</tbody>
</table>

Absorption % = 1 - \( \frac{\text{NO}_2\text{(out)}}{\text{NO}_2\text{(in)}} \) * 100%
5-3 NO₂ effect on NO absorption in caustic aqueous scrubbing

A number of experiments were performed to evaluate the effect of the reaction

\[
\begin{align*}
\text{NO} + \text{NO}_2 & \rightleftharpoons \text{N}_2\text{O}_3 \\
\text{N}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow 2 \text{HNO}_2
\end{align*}
\]

in caustic aqueous scrubbing. Experiments were conducted at the following conditions

**Flue gas:**
- Equal molar of NO and NO₂ at 300, 500, 800 ppm
- Balance: N₂
- Flow rate: 1 l/min

**Scrubbing Solutions**
- NaOH: 0.01, 0.5 M
- Volume: 1 liter

There tests were conducted at room temperature and atmospheric pressure.

The actual measurements are summarized in Tables 10 and 11. These data indicate that the presence NO₂ significantly increases NO absorption in caustic aqueous solution.
Table 10 NO₂ Effect on NO Caustic Aqueous Scrubbing

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Expt #</th>
<th>NO (in) (ppm)</th>
<th>NO (out) (ppm)</th>
<th>Abs %</th>
<th>NO₂ (in) (ppm)</th>
<th>NO₂ (out) (ppm)</th>
<th>Abs %</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1</td>
<td>361</td>
<td>136</td>
<td>62.3</td>
<td>318</td>
<td>5</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>330</td>
<td>84</td>
<td>74.5</td>
<td>295</td>
<td>11</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>325</td>
<td>125</td>
<td>61.5</td>
<td>352</td>
<td>13</td>
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<td></td>
<td></td>
<td>66.1</td>
<td></td>
<td></td>
<td>97.0</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>568</td>
<td>186</td>
<td>67.3</td>
<td>568</td>
<td>23</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>591</td>
<td>182</td>
<td>69.2</td>
<td>568</td>
<td>25</td>
<td>95.6</td>
</tr>
<tr>
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<td>542</td>
<td>167</td>
<td>69.2</td>
<td>573</td>
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<td>96.2</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td></td>
<td></td>
<td>68.6</td>
<td></td>
<td></td>
<td>95.9</td>
</tr>
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<td>354</td>
<td>58.0</td>
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<td>385</td>
<td>52.6</td>
<td>875</td>
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<td>100.0</td>
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<td>avg</td>
<td></td>
<td></td>
<td>56.5</td>
<td></td>
<td></td>
<td>98.9</td>
</tr>
</tbody>
</table>

* NaOH = 0.01 M

* \( \text{Abs(NO)} = 1 - \frac{\text{NO(out)}}{\text{NO (in)}} \times 100\% \)
## Table 11 NO₂ Effect on NO Absorption in Caustic Aqueous Solution

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>Expt #</th>
<th>NO (in) ppm</th>
<th>NO (out) ppm</th>
<th>Abs %</th>
<th>NO₂ (in) ppm</th>
<th>NO₂ (out) ppm</th>
<th>Abs %</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1</td>
<td>310</td>
<td>5</td>
<td>98.5</td>
<td>324</td>
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<tr>
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<td>2</td>
<td>355</td>
<td>19</td>
<td>94.6</td>
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<td>379</td>
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<td>336</td>
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<td>100</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td></td>
<td></td>
<td>96.2</td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>576</td>
<td>21</td>
<td>96.3</td>
<td>602</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>595</td>
<td>14</td>
<td>97.6</td>
<td>602</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
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<td>3</td>
<td>600</td>
<td>17</td>
<td>97.3</td>
<td>595</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td></td>
<td></td>
<td>97.0</td>
<td></td>
<td></td>
<td>100</td>
</tr>
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<td>100</td>
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<td>98.8</td>
<td>833</td>
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<td>100</td>
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<td>avg</td>
<td></td>
<td></td>
<td>97.9</td>
<td></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

* NaOH = 0.5 M
Oxygen Effect on NO Absorption in Caustic Aqueous Scrubbing

Oxygen is generally present in incinerator emissions because excess air is used to make sure incinerator feed is completely combusted. Since oxygen reacts with NO to form NO₂, it is important to determine its contribution to NO absorption. The following runs were performed to test this effect.

Flue gas
- NO: 300, 500, 800, 2000 ppm
- O₂: 5%
- Balance: N₂
- Flow rate: 1 l/min

Scrubbing solutions
- NaOH: 0.0001, 0.01, 1 M
- Volume: 1 liter

All runs were conducted at room temperature and pressure.

Results in Table 12 indicate that no significant change in NO absorption in caustic aqueous scrubbing occurs due to introduction of 5% O₂ into synthetic flue gas.
<table>
<thead>
<tr>
<th>NO(ppm)</th>
<th>Expt #</th>
<th>absorption %</th>
<th>Conc. of NaOH (molarity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0001</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.8</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>1.4</td>
<td>0.0</td>
</tr>
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<td></td>
<td>2</td>
<td>0.0</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
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<td>0.9</td>
</tr>
<tr>
<td>2000</td>
<td>1</td>
<td>1.3</td>
<td>0.5</td>
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<tr>
<td></td>
<td>2</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
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<td>0.4</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Absorption % = 1 - \( \frac{\text{NO(out)}}{\text{NO (in)}} \) * 100%
5-5 Oxidation of NO by NaClO₂ in aqueous scrubbing

A number of experiments were performed to evaluate the potential of sodium chlorite (NaClO₂) to oxidize NO in aqueous scrubbing under the following conditions

Flue gas
- NO: 2000 ppm
- Balance: N₂
- Flow rate: 1/min

Scrubbing solution
- NaClO₂: 0.008 M
- Na₂SO₄: 1.3*10⁻⁴ M
- Na₂CO₃: 1.5*10⁻³ M
- Volume: 1 liter

These runs were conducted at room temperature and pressure.

The first set of experiments was made to evaluate the oxidation and absorption of NO in NaClO₂ aqueous scrubbing and to ascertain the products and material balance in this reaction. Due to the impurities (18% Na₂CO₃ and 2% Na₂SO₄) in NaClO₂, the scrubbing solution had an initial pH of 10.0.

The actual measurements listed in Table 13 show that NO is quantitatively oxidized to NO₃⁻ in the liquid during the scrubbing. Hydronium ion was produced to decrease pH to 3 after the first few minutes and 1.8 at the end point of the experiment (Table 14, Figure 7). The end point is reached when NO breaks through.
Table 13 NO Oxidation by NaClO₂ in Aqueous Scrubbing

<table>
<thead>
<tr>
<th>Phase</th>
<th>Item</th>
<th>Expt #1</th>
<th>Expt #2</th>
<th>Expt #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Conc. of NO</td>
<td>2,325 ppm</td>
<td>2,075 ppm</td>
<td>2,175 ppm</td>
</tr>
<tr>
<td></td>
<td>Flow rate</td>
<td>1 l/min</td>
<td>1 l/min</td>
<td>1 l/min</td>
</tr>
<tr>
<td></td>
<td>Time (B.K.)</td>
<td>80 min</td>
<td>89 min</td>
<td>88 min</td>
</tr>
<tr>
<td></td>
<td>Moles</td>
<td>0.00759</td>
<td>0.00754</td>
<td>0.00781</td>
</tr>
<tr>
<td>liquid</td>
<td>Conc. of NaClO₂</td>
<td>0.008 M</td>
<td>0.008 M</td>
<td>0.008 M</td>
</tr>
<tr>
<td></td>
<td>Conc. of Na₂CO₃</td>
<td>0.0015 M</td>
<td>0.0015 M</td>
<td>0.0015 M</td>
</tr>
<tr>
<td></td>
<td>Conc. of Na₂SO₄</td>
<td>0.00038 M</td>
<td>0.00038 M</td>
<td>0.00038 M</td>
</tr>
<tr>
<td></td>
<td>Volume</td>
<td>1 liter</td>
<td>1 liter</td>
<td>1 liter</td>
</tr>
<tr>
<td></td>
<td>pH before</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>pH after</td>
<td>1.82</td>
<td>1.99</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>Conc. of NO₃⁻</td>
<td>480 ppm</td>
<td>460 ppm</td>
<td>480 ppm</td>
</tr>
<tr>
<td></td>
<td>Mole of Cl⁻</td>
<td>0.0080</td>
<td>0.0082</td>
<td>0.0083</td>
</tr>
<tr>
<td></td>
<td>Mole of NO₃⁻</td>
<td>0.0077</td>
<td>0.0074</td>
<td>0.0077</td>
</tr>
<tr>
<td></td>
<td>NO/ NO₃⁻</td>
<td>0.98</td>
<td>1.02</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>ClO₂⁻ / Cl⁻</td>
<td>1.00</td>
<td>1.03</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>NO/ClO₂⁻</td>
<td>0.95</td>
<td>0.94</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Time (B.K.): Break through time
Effectiveness: NO/ClO₂⁻ = 0.95
<table>
<thead>
<tr>
<th>Sample #</th>
<th>Time (min)</th>
<th>Expt #1</th>
<th>Expt #2</th>
<th>Expt #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>9.87</td>
<td>9.77</td>
<td>10.10</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>7.53</td>
<td>7.31</td>
<td>8.59</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>3.49</td>
<td>3.70</td>
<td>3.65</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>3.06</td>
<td>3.06</td>
<td>3.01</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>2.71</td>
<td>2.80</td>
<td>2.68</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>2.57</td>
<td>2.58</td>
<td>2.43</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>2.54</td>
<td>2.43</td>
<td>2.38</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>2.23</td>
<td>2.20</td>
<td>2.13</td>
</tr>
<tr>
<td>9</td>
<td>70</td>
<td>2.16</td>
<td>2.21</td>
<td>2.06</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>1.98</td>
<td>2.14</td>
<td>1.96</td>
</tr>
<tr>
<td>11</td>
<td>90</td>
<td>1.98</td>
<td>1.98</td>
<td>1.98</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>1.93</td>
<td>1.93</td>
<td>1.86</td>
</tr>
</tbody>
</table>
Figure 7 pH Change in NO Aqueous Scrubbing
The second set of experiments were performed to figure out the products formation during the experiment. Experiments were conducted at the following conditions:

Flue gas
   NO: 2,000 ppm
   Balance: N₂
   Flow rate: 1 l/min

Scrubbing solution
   NaClO₂: 0.008 M
   Na₂CO₃: 0.0015 M
   Na₂SO₄: 0.00038 M
   Volume: 1 liter

Room temperature and atmospheric pressure

Samples were taken out at fixed time interval to determine Cl⁻ and NO₃⁻ concentrations by Ion chromatography. Figure 8, derived from Table 15, indicates that the formation rates of both products are constants as the concentration of NaClO₂ changes from 0.008 to 0 Molar. This data indicates that mass transfer may be limiting the process.
Table 15  Concentrations of NO$_3^-$ and Cl$^-$ with Respect to Reaction time

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Time (min)</th>
<th>RT$^{(1)}$</th>
<th>PA$^{(2)}$</th>
<th>Conc. (ppm)</th>
<th>Conc. (M) $10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>3.09</td>
<td>3.33</td>
<td>92</td>
<td>0.26</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>3.13</td>
<td>3.74</td>
<td>108</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.51</td>
<td>0.38</td>
<td>28</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>3.13</td>
<td>5.98</td>
<td>164</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.51</td>
<td>2.49</td>
<td>140</td>
<td>0.23</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>3.18</td>
<td>8.78</td>
<td>240</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.43</td>
<td>5.28</td>
<td>284</td>
<td>0.46</td>
</tr>
<tr>
<td>5</td>
<td>52</td>
<td>3.21</td>
<td>10.41</td>
<td>290</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.41</td>
<td>7.70</td>
<td>420</td>
<td>0.68</td>
</tr>
<tr>
<td>6</td>
<td>61</td>
<td>3.20</td>
<td>10.72</td>
<td>300</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.40</td>
<td>7.98</td>
<td>440</td>
<td>0.71</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>3.23</td>
<td>10.70</td>
<td>300</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.40</td>
<td>8.51</td>
<td>490</td>
<td>0.79</td>
</tr>
<tr>
<td>8</td>
<td>75</td>
<td>3.22</td>
<td>10.69</td>
<td>300</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.41</td>
<td>8.54</td>
<td>492</td>
<td>0.79</td>
</tr>
</tbody>
</table>

(1) RT: Average retention time

RT of Cl$^-$ is 3.10 to 3.20 minute

RT of CO$_3^-$ is 5.40 to 5.50 minute

(2) PA.: Average Peak area
Figure 8 Concentration-Time Curves of NO Scrubbing

![Concentration-Time Curves of NO Scrubbing](image-url)
5-6 Oxidation of NO by NaClO₂ in Caustic Aqueous Scrubbing

In order to compare the NO absorption effectiveness of caustic scrubbing to neutral solution, several runs were made with NaOH under the following conditions:

**Flue gas**
- NO: 2,000 ppm
- Balance: N₂
- Flow rate: 1 l/min

**Scrubbing solution**
- NaClO₂: 0.01 M
- Na₂CO₃: 0.0015 M
- Na₂SO₄: 0.00038 M
- NaOH: 0.001 M
- Volume: 1 liter

All experiments were conducted at room temperature and pressure.

Result containing in Table 16 indicate that the effectiveness of NO absorption in NaClO₂ aqueous scrubbing was slightly improved (NO/ClO₂⁻ rise to 1.04) by NaOH addition.
Table 16 Effectiveness of NO Absorption in NaClO₂ Caustic Aqueous Scrubbing

<table>
<thead>
<tr>
<th>Phase</th>
<th>Item</th>
<th>Expt #1</th>
<th>Expt #2</th>
<th>Expt #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Conc. of NO</td>
<td>1,950 ppm</td>
<td>1,925 ppm</td>
<td>2,075 ppm</td>
</tr>
<tr>
<td></td>
<td>Flow rate</td>
<td>1 l/min</td>
<td>1 l/min</td>
<td>1 l/min</td>
</tr>
<tr>
<td></td>
<td>Time (B.T.)</td>
<td>104 min</td>
<td>105 min</td>
<td>100 min</td>
</tr>
<tr>
<td></td>
<td>moles of NO</td>
<td>0.0083</td>
<td>0.0083</td>
<td>0.0085</td>
</tr>
<tr>
<td>Liquid</td>
<td>Conc. of NaClO₂</td>
<td>0.0080</td>
<td>0.0080</td>
<td>0.0080</td>
</tr>
<tr>
<td></td>
<td>Conc. of Na₂CO₃</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0015</td>
</tr>
<tr>
<td></td>
<td>Conc. of Na₂SO₄</td>
<td>0.00038</td>
<td>0.00038</td>
<td>0.00038</td>
</tr>
<tr>
<td></td>
<td>conc. of NaOH</td>
<td>0.00097</td>
<td>0.00097</td>
<td>0.00097</td>
</tr>
<tr>
<td></td>
<td>Volume</td>
<td>1 liter</td>
<td>1 liter</td>
<td>1 liter</td>
</tr>
<tr>
<td></td>
<td>pH before</td>
<td>11.27</td>
<td>11.27</td>
<td>11.27</td>
</tr>
<tr>
<td></td>
<td>pH after</td>
<td>1.69</td>
<td>1.75</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>Conc. of NO₃⁻</td>
<td>510 ppm</td>
<td>520 ppm</td>
<td>510 ppm</td>
</tr>
<tr>
<td></td>
<td>Mole of Cl⁻</td>
<td>0.0083</td>
<td>0.0086</td>
<td>0.0087</td>
</tr>
<tr>
<td></td>
<td>Mole of NO₃⁻</td>
<td>0.00823</td>
<td>0.00839</td>
<td>0.00823</td>
</tr>
<tr>
<td></td>
<td>NO/NO₃⁻</td>
<td>1.01</td>
<td>0.99</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>Cl⁻/ ClO₂⁻</td>
<td>1.03</td>
<td>1.05</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>NO/ClO₂⁻</td>
<td>1.04</td>
<td>1.04</td>
<td>1.06</td>
</tr>
</tbody>
</table>
5-7 Oxygen Effect on NO Absorption in NaClO$_2$ Aqueous Scrubbing

When flue gas containing O$_2$ is bubbled through a NaClO$_2$ containing scrubber, NaClO$_2$ may react with O$_2$. In order to ascertain this effect, several runs were made at the following conditions:

Flue gas

NO: 2,000 ppm
O$_2$: 5%
Balance: N$_2$
Flow rate: 1 l/min

Scrubbing solution

NaClO$_2$: 0.01 M
Na$_2$CO$_3$: 0.0015 M
Na$_2$SO$_4$: 0.00038 M
Volume: 1 liter

All experiments were conducted at room temperature and pressure.

Table 17 shows that the effectiveness of NO scrubbing by NaClO$_2$ decreased (NO/ClO$_2^-$ drop to 0.84) when O$_2$ was present in the flue gas.
<table>
<thead>
<tr>
<th>Phase Item</th>
<th>Expt #1</th>
<th>Expt #2</th>
<th>Expt #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Conc. of NO</td>
<td>1,883 ppm</td>
<td>1,841 ppm</td>
<td>1,883 ppm</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1 l/min</td>
<td>1 l/min</td>
<td>1 l/min</td>
</tr>
<tr>
<td>Break through</td>
<td>84 min</td>
<td>90 min</td>
<td>90 min</td>
</tr>
<tr>
<td>Mole of NO</td>
<td>0.0065</td>
<td>0.0068</td>
<td>0.0069</td>
</tr>
<tr>
<td>Liquid Conc of NaClO₂</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>Conc of Na₂CO₃</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0015</td>
</tr>
<tr>
<td>Conc of Na₂SO₄</td>
<td>0.00038</td>
<td>0.00038</td>
<td>0.00038</td>
</tr>
<tr>
<td>volume</td>
<td>1 liter</td>
<td>1 liter</td>
<td>1 liter</td>
</tr>
<tr>
<td>mole of ClO₂⁻</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>NO/ ClO₂⁻</td>
<td>0.81</td>
<td>0.85</td>
<td>0.86</td>
</tr>
</tbody>
</table>
5-8 pH Effect on NO Absorption in NaClO$_2$ Aqueous
Scrubbing

Based on the results reported in section 5-6, a certain amount of NO breaks through with NaClO$_2$ scrubbing in presence of 0.001M NaOH. It was presumed that NaOH may inhibit or may lower the mass transfer coefficient of this process. In order to ascertain the veracity of this prediction, a number of experiments were performed under the following conditions

Flue gas

- NO: 2,000 ppm
- Balance: N$_2$
- Flow rate: 1 l/min

Scrubbing solution

- NaClO$_2$: 0.00008, 0.0008, 0.008, 0.08 M
- Na$_2$CO$_3$: 0.000015, 0.00015, 0.0015 and 0.015 M
- Na$_2$SO$_4$: 0.0000038, 0.000038, 0.00038 and 0.0038 M
- NaOH: 0.0001, 0.001, 0.005, 0.01, 0.1, 1 M
- Volume: 1 liter

All runs were conducted at room temperature and pressure.

Figure 9, derived from Table 18, indicate that high concentration of NaOH inhibit NO absorption in NaClO$_2$ aqueous scrubbing.
Table 18 pH Effect on NO Absorption in NaClO\textsubscript{2} Caustic Aqueous Scrubbing

<table>
<thead>
<tr>
<th>Conc. of NaOH (M)</th>
<th>Expt #</th>
<th>Per-cent Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conc. of NaClO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.00008 0.0008 0.008 0.08</td>
</tr>
<tr>
<td>0.0001</td>
<td>1</td>
<td>1 0 100 100</td>
</tr>
<tr>
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<td>2</td>
<td>2 0 100 100</td>
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<tr>
<td></td>
<td>3</td>
<td>1 0 100 100</td>
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<td></td>
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<td>1 0 100 100</td>
</tr>
<tr>
<td>0.001</td>
<td>1</td>
<td>1 0 100 100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0 1 100 100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3 0 100 100</td>
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<td>1 0 100 100</td>
</tr>
<tr>
<td>0.005</td>
<td>1</td>
<td>- - 25 100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>- - 24 100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>- - 25 100</td>
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<td>avg</td>
<td>- - 25 100</td>
</tr>
<tr>
<td>0.01</td>
<td>1</td>
<td>0 0 4 100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0 2 6 100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0 1 8 100</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>0 1 6 100</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>1 0 0 17</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0 1 0 17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1 1 1 19</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>1 1 1 18</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>0 2 0 0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0 2 1 2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4 1 0 0</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>1 2 0 1</td>
</tr>
</tbody>
</table>

$\text{NO} \text{(out)}$

Absorption \% = 1 - \frac{\text{NO} \text{(in)}}{\text{NO} \text{(out)}} * 100\%

70
Figure 9  PH Effect on NO Absorption in NaClO₂ Caustic Aqueous Scrubbing
A semibatch reactor was used to evaluate the potential of oxidizing NO with NaClO$_2$ in an alkaline scrubbing solution. The synthetic flue gas was blended from compressed gas cylinders and was continuously fed to the scrubbing solution which was the stationary phase in the reactor. The flue gas was introduced into the reactor through a polyethylene sparger located at the bottom of the reactor. Thus the bubble size was influenced by the pressure of flue gas, the size the sparger openings, and the viscosity of the scrubbing solution.

The absorption of NO by an aqueous solution of alkaline NaClO$_2$ was accomplished at room temperature and 101.3 kPa of flue gas pressure. A greenish yellow color in the solution was found after three minutes of operations and disappeared after 105 minutes. It is assumed that the color represents an intermediate in the absorption of NO. The mole ratio of the total amount of NO that flowed through the reactor to NaClO$_2$ is 0.95 at breakthrough. It should be reemphasized that 80% NaClO$_2$ was used with the rest of the starting material in solution consisting of 18% Na$_2$CO$_3$ and 2% Na$_2$SO$_4$. Thus, the initial composition of the scrubber liquid was quite alkaline. Under all conditions when NaClO$_2$ was present, the other two reagents were also present. For expediency, this fact may not be mentioned every time NaClO$_2$ chemistry is discussed.

Low concentrations of NaOH increase the NO removal
effectiveness. High concentrations of NaOH inhibited the absorption. The upper limit for NaOH concentration necessary to completely absorb NO in NaClO$_2$ aqueous solution depends on the concentration of NaClO$_2$. NO was absorbed quantitatively in 0.008 molar NaClO$_2$ aqueous solution when the concentration of NaOH was equal to or lower than 0.001 molar. The upper limit of NaOH in 0.08 molar NaClO$_2$ aqueous solution is 0.1 molar. At the upper limit concentration of NaOH, absorption can not reach 100% within the first few minutes. If the NaOH concentration is a little higher than upper limit, absorption goes to zero after a few minutes of running time.

NaOH in NaClO$_2$ aqueous solution increases the effectiveness of NO to NaClO$_2$ reactant ratio at breakthrough to 0.96 - 1.05 while 5% oxygen in the flue gas decreases it to 0.84.

Before saturation, the concentration-time curves are straight lines of different slopes. Slope of NO$_3^-$ is greater than that of Cl$^-$. The rate of formation of NO$_3^-$ is faster than that of Cl$^-$. The time between their formation is the life time of the green intermediate.

The pH value of the aqueous solution drops drastically from 10 to 3 within the first ten minutes. The solution was prepared with 0.008 molar of NaClO$_2$ and 0.0015 molar of Na$_2$CO$_3$ owing to the 18% (w/w) and 2% Na$_2$SO$_4$ impurity. The pH value of this solution is 10. After three minutes running, the reaction was carried out under acidic condition.
After NaClO₂ in scrubbing solution was used up, only two products were found in the scrubbing solution. They were NO₃⁻ and Cl⁻. The CO₃⁻² converted to H₂CO₃ when pH fell below 3. The pH value of the scrubbing solution is 1.9. Under this situation, no CO₃⁻² exist in the solution. Since no CO₃⁻² signal is found in ion chromatography.
7 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS

7-1 Conclusions

A series of experiments were performed in order to evaluate the capability of alkaline NaClO₂ aqueous solution to scrub NO by oxidizing it from synthetic flue gas. In some runs, NO₂ or O₂ were mixed into the synthetic flue gas to simulate the flue gas emitted by municipal incinerator or stationary power plant. The conclusions from this research are listed as below:

* At room temperature and atmospheric pressure, NO is not absorbed by distilled water. NaOH up to 1.0 molar does not improve this absorption.

* At room temperature and atmospheric pressure, NO₂ can be absorbed effectively by NaOH aqueous solution. A 0.5 molar NaOH aqueous solution can scrub 98% of NO₂ from flue gas at relatively low NO₂ concentration (lower than 800 ppm).

* The effectiveness of NO absorption in caustic aqueous scrubbing is greatly increased by the presence of NO₂ in the flue gas.

* 5% O₂ in flue gas does not affect NO absorption in caustic (NaOH up to 1.0 molar) aqueous scrubbing.

* NO can be oxidized effectively by NaClO₂ in aqueous solution. During scrubbing, NO is oxidized to NO₃⁻, and ClO₂⁻ converted to Cl⁻ in scrubbing solution.
* Owing to the production of HNO$_3$, pH drops sharply from 10 to 3 within ten minutes in the scrubbing of NO by alkaline NaClO$_2$ aqueous solution.

* Rates of Cl$^-$ and NO$_3^-$ formation in scrubbing solution are constants at the low concentration scrubbing process as the concentration of NaClO$_2$ changes from 0.008 molar to 0 molar.

* Low concentration of NaOH increase the effectiveness of NO absorption in NaClO$_2$ aqueous scrubbing solution by 7%, while concentrations higher than upper limit decreases or inhibits its absorption.

* Effectiveness (NO/ClO$_2^-$ ratio) decrease from 0.95 to 0.84 when 5% O$_2$ in presence of flue gas.

**7-2 Recommendations for future works**

The results of this program clearly indicates the utility of NaClO$_2$ for NO$_x$ emission control. The best conditions of chemical reaction of NO$_x$ in NaClO$_2$ and aqueous scrubbing can be reached from the results presented in this thesis. However, to develop the engineering data that is essential for scale-up, pilot plant studies are needed. Some critical factors which need to be studied in pilot plant process are listed below:

* Rate of NO absorption in alkaline NaClO$_2$ aqueous solution in pilot plant conditions.

* The overall mass transfer coefficient and interfacial area
of pilot plant process.
* How does temperature affect this process in pilot plant conditions
* How do other flue gas components affect the NO absorption in NaClO₂ aqueous scrubbing.
* Optimization should be assessed.
* How to treat the scrubbing solution (pH of 1.8 and NO₃⁻).

The purposes of this program should be to completely remove NOₓ from flue gas and the effect of scrubbing solution must be minimized to meet the regulations at the same time.
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