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ABSTRACT

Alkaline solutions of tert-butyl hydroperoxide (TBHP) selectively remove NO from simulated flue gasses. The investigation was conducted in a bubbling scrubber. NO removal efficiency of the scrubbing solutions was evaluated as a function of various operating parameters such as pH, oxidant concentration, oxidant to base mole ratio, residence time, temperature and flue gas compositions.

Alkaline solutions of TBHP show promise of being an economical choice for the selective removal of NO from flue gas. Solutions containing 0.2 M TBHP, 0.03 M NaOH (pH 12.5), and 1 minute NO residence time remove NO to below detectable levels at 53 °C. The source of alkalinity including KOH, NaOH and Ca(OH)₂ was not a significant factor. NO removal increased with increasing ratio of alkali to TBHP, residence time, and temperature up to 80 °C. Above 80 °C vaporization of the reactant becomes significant. The ratio of alkali to TBHP resulted in a curve starting from 0.0004:1 where 100% removal was not observed to a plateau starting at 1:1 where 100% removal was observed at 75 °C. A nadir is obtained between a mole ratio of 0.005:1 to 0.03:1. TBHP solutions containing calcium hydroxide as the source of alkali (whose corresponding sulfite salt is not soluble) show little or no sulfite reaction and may be a good choice for scrubbing systems where SO₂ is present. Calcium hydroxide solutions can oxidize and absorb NO to below detectable levels with 0.2 M TBHP, 0.0056 M Ca(OH)₂ (pH 11.75), and 1 minute residence time at 63 °C.

The end products obtained from the oxidation of NO with TBHP are tert-butanol, and inorganic nitrite and nitrate.

This chemistry lends itself to application in conventional flue gas desulfurization (FGD) scrubbers that use lime or limestone slurries as the scrubbing medium for SO_x control. TBHP would be added to the FGD scrubber as an additive. This approach would convert an existing FGD scrubber to a SO_x/NO_x control unit at a fraction of the cost for separate NO_x control.

**CONTROL OF NO_x IN ALKALINE MEDIA WITH TERTIARY BUTYL
HYDROPEROXIDE**

by
David R. Edwards

**A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
In Partial Fulfillment of the Requirements for the Degree of
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APPROVAL PAGE

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This thesis is dedicated to my parents for their never ending support.

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CHAPTER 1

INTRODUCTION

Compounds of Nitrogen, both inorganic and organic, play an important role in the chemistry of the atmosphere. Nitrogen exists primarily in the relatively inert diatomic state (N_2), but through natural and anthropogenic means is converted to the oxides of nitrogen (NO_x). The principal forms of NO_x are NO and NO_2 and are formed from atmospheric nitrogen and oxygen during high temperature combustion. They are also formed from the combustion of nitrogen compounds found in fuels and the incineration of garbage and other wastes. More than 90% of NO_x emitted from stationary sources is in the form of NO. NO is insoluble in water. This leads to two serious problems: (a) once released, NO is not washed out by rain, and (b), current control devices that rely on aqueous removal are not effective. However, NO continues to react in the atmosphere to form NO_2 , which reacts with hydrocarbons in the presence of sunlight to produce smog and ozone. In 1985, anthropogenic sources in the United States contributed 19 Tg of NO_x to the atmosphere. Emissions of NO_x are believed to have risen steadily from 1900 to 1970 due to the rise in fuel consumption, particularly from power plants and automobiles (1).

1.1 NO_x Formation and Sources

Fuel composition and combustion temperature are key factors in the production of nitric oxide (NO). Due to this variability, total NO_x emissions are difficult to estimate and there

are large uncertainties associated with them. It is estimated that about 70-90% of atmospheric NO_x emissions are from anthropogenic sources (2).

1.1.1 Lightning

The single primary source of natural NO_x is due to the effect of lightning on atmospheric nitrogen and oxygen. The temperature of the column of air immediately surrounding the lightning bolt is dependent on the energy deposition of the lightning. A typical lightning bolt has a energy deposition of 10^5 J/m. The column of air immediately surrounding such a bolt will rise to about 30,000 K. At temperatures greater than 2,300 K, NO is in thermodynamic equilibrium with atmospheric nitrogen and oxygen. As the temperature of the air drops below 2,000 K, the equilibrium NO concentration freezes and does not decompose to its constituent components.

The total global production of NO due to lightning is a product of two factors:

NO yield per lightning energy output, or amount of NO per flash, and
lightning flash frequency (3).

This major source of natural NO_x accounts for 1/3 of the natural NO_x produced (4).

1.1.2 Soil Microbial Activity

It has been found through field and laboratory studies that soil dwelling microorganisms also generate significant quantities of NO. To determine the rate of NO production, a series of laboratory experiments had been conducted using two of the most common nitrogen manipulating bacteria *Nitrosomonas Europaea* and *Alcaligenes Faecalis*. The

result indicates that NO production is a byproduct of the oxidation of ammonium cations to nitrite and nitrate anions (3). Sources from the soil account for about 2/3 of natural NO_x (4).

1.1.3 Fuel Combustion

Nitric oxides (NO_x) are generated in combustion processes that employ air as the oxidizer. At flame temperatures, the reaction between nitrogen and oxygen is rapid resulting in the formation of nitric oxide (NO). The mechanism of formation for NO from N₂ and O₂ follows the chain reaction sequence first suggested by Zeldovitch (5) and confirmed by shock tube studies on N₂-O₂ mixtures (6).

The chain reaction sequence is shown in equations 1.1 through 1.3,



where M is a third body. The quantitative kinetics of this system was solved by Shaw in closed form in 1973 (7).

1.2 Effects of Nitrogen Oxides

Nitrogen oxides (NO_x) are responsible for many serious environmental and health problems, such as stratospheric ozone depletion, tropospheric ozone formation, acid precipitation, respiratory diseases, etc. These problems will be discussed later in this section.

1.2.1 Tropospheric Ozone Formation

Increasingly, air pollution alerts are issued, warning the public of excessive ozone in the air. The principal culprit in the formation of ozone is NO from combustion sources. In addition, peroxyacetyl nitrate (PAN) increases the rate of ozone formation by releasing NO₂, as well as transporting the problem downwind before decomposing into peroxyacetyl radicals and NO₂ (8). Ozone has an adverse effect on the respiratory health of the very young and the elderly. NO₂ is used as a standard in health studies rather than NO for the reason that, given enough time, all the NO will be oxidized to NO₂ in the atmosphere. The reaction rate between nitric oxide and oxygen is very slow, but will follow the reaction given in equation 1.4 (9).



The kinetics are given in Shaw (17).

1.2.2 Acid Precipitation

Acid precipitation is implicated in the increasing acidity in poorly buffered soils (10). It is also suspected in damaging vegetation as well as altering biological communities, surface waters and natural structures. In 1980, the U.S. National Acid Precipitation Assessment Program (NAPAP) was implemented to conduct research on the causes and effects of acid deposition. There were two chief goals for NAPAP: First was to address the many deficits in our understanding of the problem. The second was to develop means for controlling acid precipitation and evaluating the performance of these methods (11).

1.2.3 Health Effects

Nitrogen oxides themselves are generally not thought to be very active biologically. It has been found that at exposures above a few ppm, NO₂ can cause lung damage of several types. It may cause bronchial damage similar to, but less severe than, SO₂ as well as acute pulmonary edema, similar to damage characteristic of exposure to ozone. However, since the atmospheric concentration only rarely even reaches one half a ppm (941 ug/m³), it had been assumed that there were no health effects of NO₂. This view has been put into doubt since findings from a major epidemiological study in Chattanooga (12) indicated that significant health effects can be attributed to NO_x. It was discovered that populations of people who lived in the vicinity of a TNT manufacturing plant suffered from pulmonary constriction and greater incidence of respiratory illness compared to the rest of the community. The areas corresponding to the illnesses were found to have NO₂ levels ranging from 0.06 to 0.109 ppm (113-205 μg/m³), similar to levels occasionally experienced in many other cities. As a result, we need to reconsider how we evaluate NO₂ levels (13).

1.3 NO_x Control Technologies

NO_x control devices or low NO_x operating procedures are an absolute necessity in order to comply with federal and local regulations and reduce environmental problems.

Recently, a variety of control methods for NO_x control have been developed. There are two basic types of control methods: the first type is simply modifying the combustion process, the second are add-on devices for flue gas treatment. These processes are summarized on Table 1 below (15).

Table 1.1 Comparison of Several NO_x Emission Control Techniques.

	EFFICENCY %	RELATIVE COST
Combustion Modification:		
(LNB) Low Nox Burners	30-50%	Moderate
(FGR) Flue Gas Recirculation	20-30%	Moderate
(LEA) Low Excess Air	20%	Low
(OFA) Overfire Air	15-30%	Low
(BOOS) Burners Out Of Service	50%	Low
Flue Gas Cleaning:		
(SNR) Thermal De-NO _x	30-80%	Moderate
(SCR) Selective Catalytic Reduction	50-90%	High
Scrubbing System	> 90%	High*

1.3.1 Combustion Modification

Low NO_x Burners (LNB) have been developed by most boiler/burner manufacturers for NO_x control in their product. There is a great deal of variability between each product but generally all have certain things in common: First they modify the means of introducing air and fuel and slow the rate of mixing, and second they reduce O₂ availability in critical NO_x forming zones. In addition they may also include Over Fire Air (OFA), Staged Combustion, and/or Flue Gas Recirculation (FGR). At moderate cost to the operator, a 50% reduction in NO_x emissions can be obtained (16).

Staged Combustion involves fuel rich combustion with 70% of the stoichiometrically required air followed by cooling and burnout of the other 30% of the fuel (16).

Flue Gas Recirculation (FGR) is a method that can be applied to oil, gas, coal fired boilers, and automobiles. It may be applicable to waste regeneration plants as well. This technique is a method of flame quenching that reduces flame temperature and excess O₂

and thus reduces thermal NO_x formation. Essentially some exhaust gasses are mixed with incoming air and sent through the boiler again. Some modifications are required to be installed on the boiler to implement this technique, but costs are modest unless there is great difficulty in installation. A NO_x control rate of 20-30% can be expected with this method (16).

Over Fire Air (OFA) is a means of air staging where 10-20% of the combustion air is introduced above the last set of burners or above the grate in a stoker fired burner. This method requires precise placement of the air injection ports and has many other practical considerations in order to be effective. This method alone can achieve NO_x control of about 15-30% but is usually combined with FGR or LNB (16).

Low Excess-Air (LEA) is basically a boiler optimization strategy that regardless of NO_x considerations should be employed as standard optimization procedure. As a NO_x control method, it basically addresses the fact that high excess air levels are the fundamental cause of high NO_x emissions. Implementing LEA primarily requires operating the boiler at the lowest excess air level that is safe, efficient and cost effective. It is not likely to require capital outlays, rather just fine tuning current operations. Material problems can occur with this technique due to higher operating temperatures. LEA can provide about 10-20% control of NO_x (16).

Burner Out Of Service (BOOS) is a means of "fuel biasing" in multiple burner oil/gas fired boilers. It is an easy method to employ, requiring little or no capital expenditure. To implement, the operator simply turns off the flow of fuel to the top row of burners and allows air to go in. The balance of fuel is redirected to the lower burners. This is a crude

form of air staging mentioned above (OFA) and can achieve NO_x control of up to 50%. It is not thought to be appropriate for coal fired burners (16).

Fuel Biasing With this method, the combustion in the furnace is divided into two zones, the upper zone and the lower zone. The lower zone is burned fuel rich to reduce the formation of NO_x . The upper zone conversely is fuel lean to complete the burnout. This method is really a more refined BOOS system . NO_x control of around 20% can be expected using this method (16).

Reburning involves creating a second oxidizing zone downstream from the primary zone. The fuel for this zone must be low in nitrogen so either natural gas or oil are generally used. The second zone is burned substoichiometrically. This creates an area with many hydrocarbon radicals which provide a favorable path to convert some of the NO back to N_2 . This method works with all primary fuels and works best when combined with LNB. A combined reburning/LNB system could reach 75-90% NO_x reductions (16).

Water/Steam Injection This method is mostly used in gas turbines and although it can reduce NO_x emissions by around 70%, it is associated with an increase in carbon monoxide and unburned hydrocarbon emissions. On the economic side, fuel consumption increases 5% (to vaporize the water) and maintenance costs increase. However, the mass throughput through the turbine increases, raising the output and reducing cost. It is rarely used in oil/gas fired boilers (16, 17).

1.3.2 Flue Gas Treatment Techniques

Selective Non-catalytic Reduction (SNR): This method involves the injection into the flue gas, ammonia, urea, or some other nitrogen containing compound that will reduce NO_x to water and N_2 . Ammonia and urea are, due to relative cost, the most frequently used compounds. They both require an operating temperature of 930-990 °C to be effective. Of the two compounds urea overall seems to be somewhat simpler to use and handle. It requires fewer injection ports, less complicated equipment to use it, and it comes as a solid or aqueous solution rather than a toxic gas. The SNR process is prone to the production the low melting salts of ammonium sulfite and ammonium sulfate particularly when SO_3 levels are high which foul the heat transfer area. Ammonia emissions are also a concern. SNR has been shown in the development phase to control NO_x by as much as 80% (13, 18).

Selective Catalytic Reduction (SCR): is a process very similar to SNR except that it employs a catalyst to allow the reactions to occur at a lower temperature (300-400 °C). SCR uses a Vanadium, Titanium or Platinum catalyst, on a variety of substrates, to speed the rate of the reaction of the ammonia with NO_x . Although SCR is capable of removing up to 90% of the NO_x formed, it has some problems associated with it. One problem is the relative short life span of the catalyst and costs associated with replacing it. Another is the tendency of the catalyst to promote the formation of ammonium sulfates and for the tendency for ammonia to escape unreacted. A major problem is plugging of the catalyst in coal combustion and poisoning due to SO_2 . At the current time, SCR represents the best NO_x control system available for industry (16).

Flue Gas Scrubbing There are a number of scrubbing processes that have been proposed to remove NO_x from flue gas. All of these methods require the use of expensive oxidizing agents that may present a disposal problem (16). The great advantage of using oxidants within the scrubber is that it will not require the addition of any further equipment if the oxidant is effective in the alkaline conditions that are already used for SO_x control (18). Many oxidizers have been tested including acidic H_2O_2 and sodium chlorate but suffered from incompatibility with current systems or sulfite reaction with the oxidant. Add-on devices are generally applicable to all fuel types since they deal with gasses in the flue pipe rather than the combustion area.

CHAPTER 2

LITERATURE REVIEW

In most instances the avoidance of creating a pollutant is the best course of action for compliance with regulatory restrictions. In the case of NO_x , it is not a realistic alternative. Combustion with air will almost certainly result in the formation of NO_x . With current technology, the best way to “not create” NO_x is by combustion modification or, as discussed in a book by Bonn and Baumann (19), to replace N_2 with CO_2 in the combustion chamber results in drastic reductions in NO_x and N_2O . However, combustion modification rarely reaches 50% efficiency. Also, combustion modification techniques to reduce NO_x formation can produce greater levels of other pollutants such as CO and/or reduce fuel efficiency. In addition, certain non conventional fuels, such as garbage, are very difficult to burn cleanly.

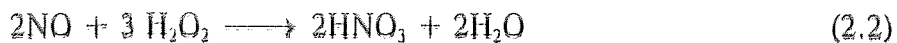
With the increasing importance of NO_x control for regulatory compliance, a suitable means of absorption similar to that for the removal of sulfur dioxide would be a very desirable alternative solution to SCR mentioned in the previous chapter. Unfortunately, the low solubility of NO in current wet scrubbing absorbents render them ineffective for the control of NO. To make scrubber absorbents effective for the control of NO requires the addition of a strong oxidant to oxidize the NO from either the gas phase or the liquid phase to more soluble oxides of Nitrogen. (NO_2 , N_2O_3 , HNO_2 and HNO_3)

2.1 NO Absorption into Solution Accompanied by Oxidation Reaction

It is very important, when choosing an oxidant to enhance the absorption of NO into solution, to select an oxidant that is highly reactive. This is necessary due to the low reactivity of NO oxidizing to NO₂. In recent years, there have been a number of promising oxidants employed by researchers to react with NO. Among these are: hydrogen peroxide, potassium permanganate, sodium chlorite, peroxyacids and organic peroxides.

Sodium Sulfite: Shaw (9) studied the effectiveness of sodium sulfite solutions to remove NO. He found that dilute solutions were effective in removing NO₂ but not NO.

Hydrogen Peroxide: Experiments using H₂O₂ to oxidize NO were conducted by several researchers. Takahashi, et al., (20) reported 95% conversion of NO in a gas phase reaction of 1:1.3 ratio of NO to H₂O₂ at 400 °C. Baveja, et al., (21) studied the reaction kinetics of NO in an H₂O₂ solution in the liquid phase. They report that the rate of reaction for both NO and H₂O₂ to be first order. The second order rate constant is 8.42 * 10⁵ cm³/g-mol·sec with an activation energy of 13.7 kcal/g-mol at 30 °C. The reaction involves the following steps:

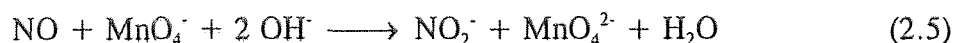


Potassium Permanganate/Sodium Hydroxide: Sada, et al., (22) and Uchida, Kobayashi and Kageyama (23) conducted experiments using aqueous solutions of KMnO₄ with and

without NaOH.. The reaction was reported to be first order for both reactants. The reported chemical reaction for the neutral solution is (22):

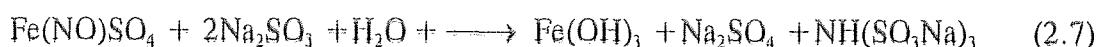
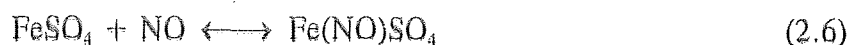


The chemical reaction for the $\text{KMnO}_4/\text{NaOH}$ system at high pH is given below:

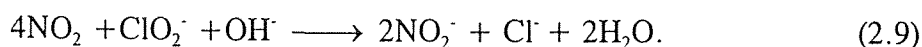
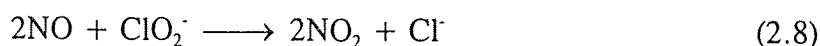


At low alkalinity it was discovered that the formation of MnO_2 formed a reaction inhibiting layer reducing the absorption of NO. At higher alkalinity there was no formation of MnO_2 and the rate of reaction remained constant.

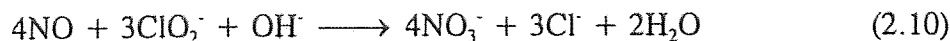
Sodium Sulfate/Ferric Sulfate: Uchida, et al., (23) conducted experiments using a solution of $\text{Na}_2\text{SO}_3/\text{FeSO}_4$ to react with NO. They report that NO absorption increases with the concentration of Na_2SO_3 up to a maximum concentration of $1 \times 10^{-4} \text{ gmol/cm}^3$. Above this concentration, absorption decreases due to an increase in pH which causes $\text{Fe}(\text{OH})_2$ to form and precipitate out. The chemical equations for the reactions are given below:



Sodium Chlorite: Yang (15) and Sada, et al., (24,25) studied NO absorption in aqueous solutions of NaClO_2 and NaOH. The reaction between NO and ClO_2^- in alkaline solution is reported as:



The overall reaction can be reduced to:



The dominant reaction was discovered to be parallel reactions involving oxidation and hydrolysis and is second order with respect to NO_2 . The order of reaction for ClO_2^- was derived as unity for chlorite concentrations greater than 1.0 M. The order of reaction for NO when chlorite concentrations are 1.0 M or greater is 2 when the interfacial concentration of NO is above 5×10^{-7} to 2×10^{-6} mol/dm³. Below this transition region, the order of reaction approaches unity. C. L. Yang (15) and Sada, et al., (25) reported that increasing the NaOH concentration resulted in a decreased absorption of NO due to a neutralization reaction. The inhibitory effect of NaOH is dependent on the concentration of NaClO₂ in the solution. The upper limit of NaOH in a 0.08 M NaClO₂ solution is 0.1 M .

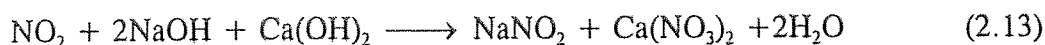
Peracid Solution: Peracids, which are generated when carboxylic acids are reacted with concentrated hydrogen peroxide, have been demonstrated as effective for NO removal by Littlejohn, et al., (26) The NO oxidation reactions are given below:



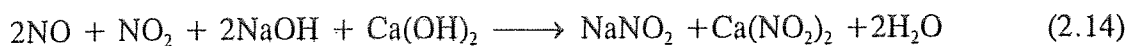
It was observed that the best NO conversion was obtained at higher temperatures > 55 °C and a pH between 3.5-5. Unfortunately under these conditions peracids become unstable and significant losses occur due to decomposition.

Soda Lime: Ishibe, et al., (27) reported that soda lime solutions are effective in removing NO₂ from a gas stream. It was also discovered that the system would also remove NO on

a 1 to 1 ratio with NO_2 where both coexist in a gas stream. In gas streams where NO_2 does not coexist with NO the absorption of NO is minimal due to the low solubility of NO . The absorption of NO_2 in soda lime is as follows:

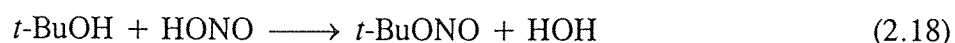
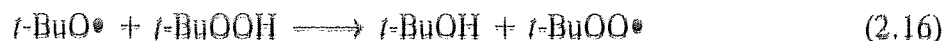
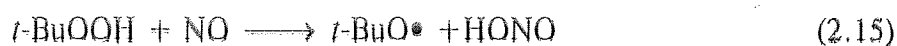


If NO is also present the following reaction will occur:

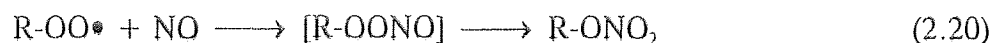
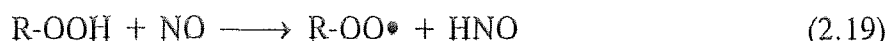


The soda lime system would be practical to employ as a NO control device for such applications where NO_2 represents a large percentage of the NO_x in the flue gas.

Organic Hydroperoxide: Sheldon and Kopczewski (28) conducted an investigation that was primarily interested in the oxidation of concentrated NO and not in air pollution. In their investigation of nitric oxide oxidation in a 0.5 M tert-butyl hydroperoxide (TBHP) in benzene solution, they reported that NO is rapidly oxidized by TBHP. The reaction ultimately yields equal quantities of tert-butanol (TBOH) and tert-butyl nitrate (TBNO_2). The reaction includes intermediate products that eluded earlier researchers. The reaction sequence goes as follows (A dot after a compound symbolizes a free radical):



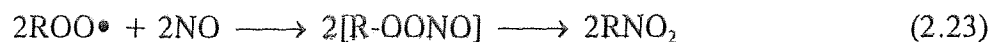
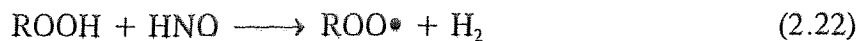
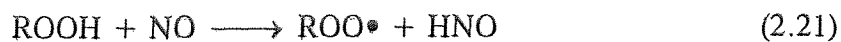
Carlsson, et al., (29,30) reported that the reaction of NO with concentrated solutions of hydroperoxides generated from oxidized polyolefins resulted in the formation of only organic nitrates as the dominant product and less than five percent nitrite. However, in dilute solutions of these hydroperoxides, the product is equimolar amounts of organic nitrate and nitrite. Carlsson, et al., (29,30) propose that, rather than an initial attack by NO of the O-O bond in the hydroperoxide as proposed by Sheldon and Kopczewski (28), at high hydroperoxide concentrations, the hydrogen is abstracted by the following reactions:



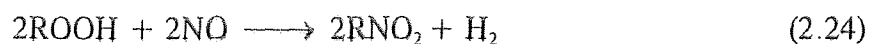
The detection of pale yellow-green gas after the NO reaction with the oxidized polyolefins is consistent with the formation of HNO.

Permuter, et al., (31) and Huihong Ao (32) studied the selective removal of NO from gas streams using 3,6-dimethyl-3-octyl hydroperoxide, p-menthanyl hydroperoxide, pinanyl hydroperoxide and cumene hydroperoxide solutions in n-hexadecane. The parameters of temperature, residence time and hydroperoxide concentration were evaluated for their influence on NO oxidation. It was found that NO oxidation increased as all the evaluated parameters increased. Although all the evaluated hydroperoxides were effective in oxidizing NO, cumene hydroperoxide was determined to be the most efficient in this role. In the evaluated system, NO reacted with the hydroperoxides to form alkyl nitrates. These can be easily hydrolyzed with ammonium hydroxide to yield ammonium

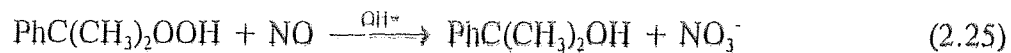
nitrate and the corresponding alcohol. The equations for the reaction of the hydroperoxides with NO are given below:



The overall reaction can be reduced to:



NO oxidation from gas streams was studied in greater detail by Chen (33) who reported a maximum NO removal of 70% at 100 °C and 80 second residence time. The organic nitrates produced were hydrolyzed to inorganic nitrate and nitrite anions via alkaline hydrolysis. The reaction is given below:



CHAPTER 3

EXPERIMENTAL

This chapter will discuss the materials, methods and safety measures employed in this research.

3.1 Chemicals

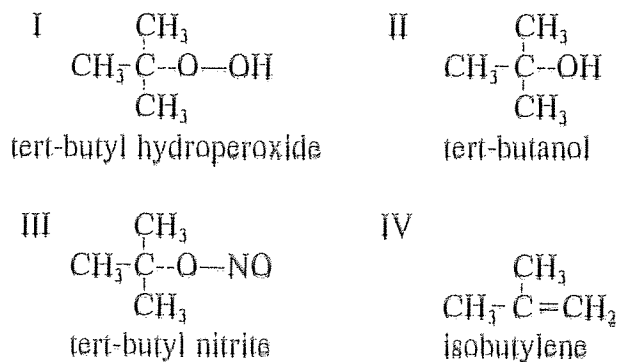
Tert-butyl Hydroperoxide: Tert-butyl hydroperoxide (TBHP) was obtained in commercial grade under the trade name Luperox TBH70X from Elf Atochem North America Inc., Philadelphia PA. The TBHP was obtained 70% pure and used without further purification. The impurities consist of tert-butanol and water. TBHP is moderately soluble in water. TBHP is stable at ambient temperatures, but decomposes to tert-butanol and oxygen with increasing rapidity above 86 °C. At elevated temperatures (140 °C +) TBHP decomposes to give acetone, isobutylene, methanol, tert-butanol, formaldehyde, water and methane (36).

Alkaline Reagents: The sodium hydroxide was commercial grade from Pfaltz & Bauer, Inc.. The potassium hydroxide, calcium hydroxide and magnesium hydroxide were all reagent grade from Aldrich Chemical Co., J. J. Baker Chemical Co. and Fisher Scientific Co.

Gases: The nitric oxide (NO) and sulfur dioxide (SO₂) with the balance in nitrogen were obtained from Matheson Gas Co. The NO cylinder also had small quantities of NO₂ as an impurity, the concentration of which was less than 10% of the NO concentration.

Iodometry Reagents: Sodium iodide, isopropanol, glacial acetic acid and sodium thiosulfate were used in the iodometric titration method described in Mair and Graupner, (34). Iodometry was used to determine the concentration of TBHP in the scrubbing solutions. All the reagents were purchased from Aldrich Chemical Co.

Standard Reagents Used for Ion Chromatography (IC) and Gas Chromatography-Flame Ionization Detector (GC-FID): Sodium nitrite, sodium nitrate, sodium sulfate were used as standards for the inorganic products of NO_x . These chemicals were obtained from EM Science and Fluka Chemika. Tert- butanol, tert-butyl nitrite and isobutylene were used as GC-FID standards to quantify or qualify the distribution of organic products. They were purchased from Fisher Scientific, Aldrich Chemical Co., and Matheson Gas Co. respectively. The structure of these chemicals are shown below:



3.2 Experimental Setup and Procedure

3.2.1 Experimental Setup

A schematic diagram of the experimental equipment is shown in Figure 3.1 (35). The apparatus consisted of two Ace Pyrex® glass columns 50 mm I. D. by 1.2 m in length

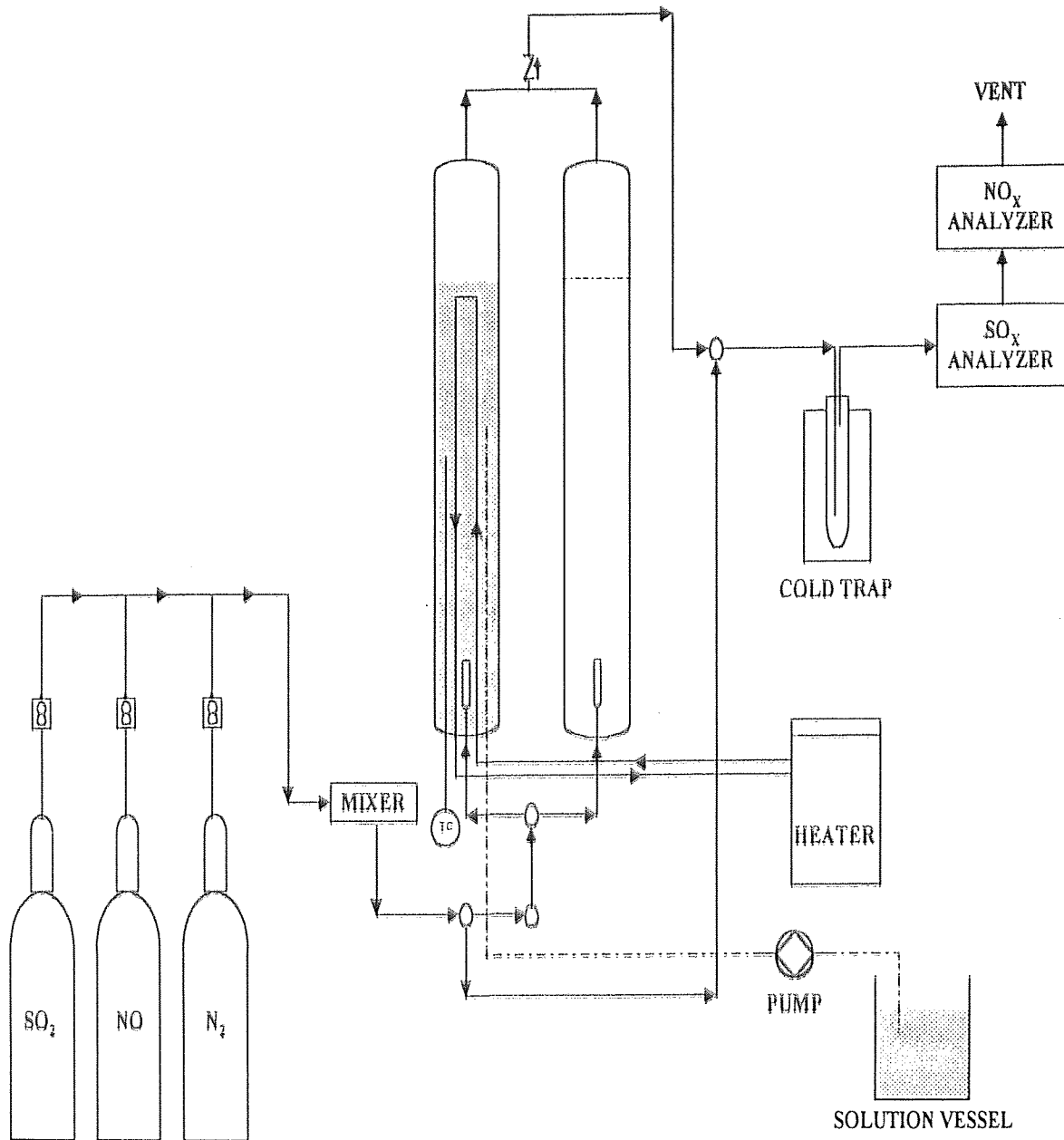


Figure 3.1 Diagram of Experimental Apparatus.

and nominal capacity of 2.35 dm³. These columns were capped on both ends with teflon caps. The caps on the bottom were drilled to allow the insertion of diffusers, heating coil, thermocouple and sampling port. On the top, only an exit port was drilled. The simulated flue gas was introduced to the scrubbing solution through the diffuser to assure a high surface area to volume ratio between the gas and liquid phase. One quarter inch Stainless Steel tubing was inserted into the scrubber as a heat exchanger. A temperature-controlled hot water bath, equipped with a Neslab® RTE-110 circulation pump, was attached to the tubing to heat and maintain the temperature of the scrubbing solution to $\pm 1^\circ\text{C}$. The temperature of the solution was monitored with an Omega® type K thermocouple (Chromel, vs., Alumel) inserted into the scrubbing solution through the bottom cap. To capture water vapor and volatilized organic compounds, a combination of an impinger with an alkali bath and cold trap(s) were put in place along the exit tubing. The gas to be reacted was supplied from cylinders containing NO or SO₂ with the balance being nitrogen. The gasses were delivered to the columns, SO_x and NO_x analyzers and then to the building exhaust system via ¼ inch polypropylene tubing. The rate at which the gas was fed to the reactors was regulated by Porter® series 100F or 200F mass flow controllers before the gas went to the columns. The mass flow meters were calibrated with a bubble meter primary standard and were operating at $\pm 1\%$ of mass flow.

3.2.2 Experimental Procedure

A sample of 70% TBHP was weighed and dissolved in a volumetric flask containing either sodium, potassium or calcium hydroxide. The solution was brought to the desired volume and transferred to an Erlenmyer flask with a stirring rod and the pH was

measured while the solution was being stirred. The concentration of TBHP was determined by iodometry. A known volume of scrubbing solution was introduced to the scrubber and heated to the desired temperature by circulating hot water through the stainless steel coil inside the scrubber. The temperature inside the scrubber was monitored by a type K thermocouple. While the solution was being heated to the desired temperature, nitrogen was sent through the scrubber to purge out residual oxygen and to speed heating by mixing. After heating, a sample of the solution was removed and the concentration of TBHP was determined by iodometry. The gas flow was transferred, by way of a three way valve, to the reference column and the N_2 was turned off and the NO or SO_2 containing gas switched on to determine the concentration of NO or SO_2 after going through the reference scrubber with deionized water. The reference column is used to measure the absorption, if any, of deionized water. The three way valve was then switched to the active scrubber and the experiment started. Periodically a sample of the scrubbing solution would be withdrawn to measure the change in pH, TBHP concentration and for later analysis by ion chromatography (IC) and GC-FID.

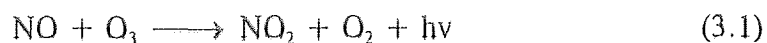
3.2.3 Safety

Most of the chemicals employed in this study are considered hazardous to human health when inhaled as a gas or vapor or by contact with the skin. To help prevent inhalation hazard chemicals were handled in a ventilation hood. Gasses were vented into a port connected to the local exhaust system. Nitrile gloves were worn to prevent skin contact with the scrubbing reagents and solutions.

3.3 Flue Gas Analysis

The change in concentration of NO, NO₂ and SO₂ during scrubbing experiments were continuously monitored by a Thermoelectron® chemiluminescent model 10 AR NO/NO_x analyzer and a Rosemount® model 890 UV SO₂ analyzer. Both instruments were calibrated before each experiment with known concentrations of NO, NO₂ and SO₂ in nitrogen.

Chemiluminescent NO/NO_x Analysis: The reaction of NO with O₃ yields a photon of light in a specific wavelength unique to this reaction as illustrated below:



The ozone required for the reaction is generated as needed by passing air or pure oxygen through a high voltage arc ozone generator within the analyzer. To measure the NO concentration, the sample gas is mixed with the ozone in a reaction chamber and the resulting light is passed through a monochromator to the photomultiplier tube to the detector. The monochromator allows only a narrow band of wavelengths specific to reaction (3.1) to reach the photomultiplier tube. The output from the photomultiplier tube is directly proportional to the concentration of NO in the sample.

The chemiluminescent reaction is selective for only NO. To measure NO₂, the sample must first pass through a high temperature converter that reduces the NO₂ to NO. Thermal conversion occurs at 670 °C. The chemiluminescent reaction is then proportional to the concentration of NO and NO₂ collectively called NO_x.

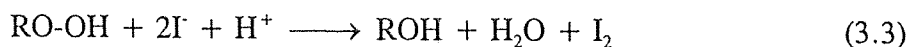
Ultraviolet SO₂ Analysis: The Rosemount® model 890 UV analyzer is designed to quantify the concentration of SO₂ in a continuous sample stream. This instrument can measure SO₂ concentrations from 50 - 5,000 ppm. The UV source emits a pulsed beam of energy to a beam splitter. Each beam is then directed to one of two pairs of detectors, one pair before and one pair after the sample cell. The pair of detectors before the sample cell are designated sample before [S_b] and reference before [R_b]. Similarly the detectors after the cell are designated sample after [S_a] and reference after [R_a]. The detectors S_a and S_b receive energy in the 265 - 310 nm wavelength region and the detectors R_a and R_b in the 310 - 355 region. In this way the detectors measure the SO₂ concentration while simultaneously correcting for NO₂ and UV lamp fluctuations. The difference between the detector determinations gives the SO₂ concentration according to the following formula:

$$SO_2 = [f(R_b) - S_b] - [f(R_a) - S_a] \quad (3.2)$$

Where f is the attenuation factor for the reference signal adjusted to compensate for NO₂ interference.

3.4 Determination of Tert-Butyl Hydroperoxide by Iodometric Titration

The method developed by Mair and Graupner (34) was employed for the quantitative determination of TBHP in the scrubbing solutions. The iodide in the method reacts stoichiometrically with hydroperoxides liberating deeply colored iodine which can be titrated to a colorless endpoint with thiosulfate. The reaction is given below:



The procedure was performed by mixing 40 cm³ reagent grade isopropanol with 2 cm³ acetic acid and 5 cm³ sample in a 250 cm³ two armed round-bottom flask and heated to reflux. When the mixture began to reflux, 10 cm³ of NaI/Isopropanol reagent containing 2 grams of NaI was added and allowed to reflux for 5-10 minutes. Five cm³ of MilliQ[®] water was added at the end of refluxing. The solution was then cooled and 10 cm³ was withdrawn and titrated from brown to a colorless endpoint with a 0.1 M sodium thiosulfate solution. Blank titrations were performed using the method outlined above but using water in the place of the sample.

3.5 Scrubbing Solution Analysis

The scrubbing solutions required no further preparation other than dilution for analysis.

3.5.1 Analysis by Ion Chromatography

A Waters[®] ion chromatograph equipped with a Waters[®] autosampler, a Waters[®] 484 UV detector and a Waters[®] 434 conductivity detector were used to analyze the inorganic nitrite, nitrate and sulfate ions generated by the scrubbing experiments. To analyze using this equipment it is necessary to make the mobile phase by dissolving 0.1008 g NaHCO₃ (1.2 mM) and 0.1272 g Na₂CO₃ (1.2 mM) per dm³ of MilliQ[®] water, filter through a 0.2 μm filter and degas for 30 minutes using a vacuum and an ultrasound bath. The flow rate for the mobile phase was 1 cm³/min. The column was a ion exchange 4.6 x 75 mm IC-Pak Anion HR. A suppresser cartridge was installed before the mobile phase flowed to the conductivity detector. The UV detector was set at 214 nm to detect nitrate and nitrite. Calibration curves for nitrite, nitrate and sulfate are shown in figures 3.2, 3.3, and 3.4

respectively. The retention times for the sodium salts of NO_2^- , NO_3^- and SO_4^{2-} were, in order, 5.93 min, 9.10 min, and 14.48 min..

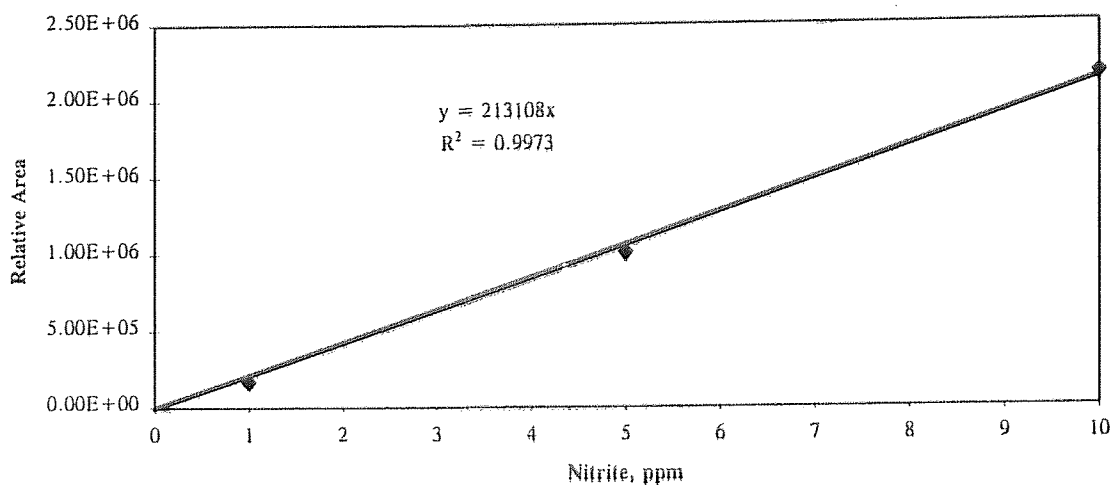


Figure 3.2 Calibration Curve for Nitrite (UV Detector)

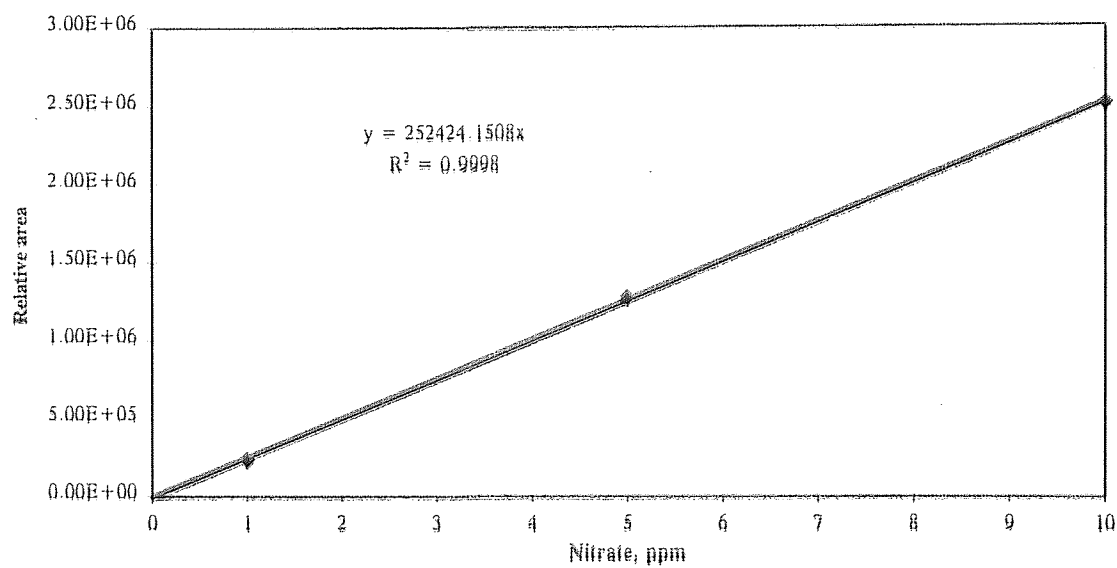


Figure 3.3 Calibration Curve for Nitrate (UV Detector)

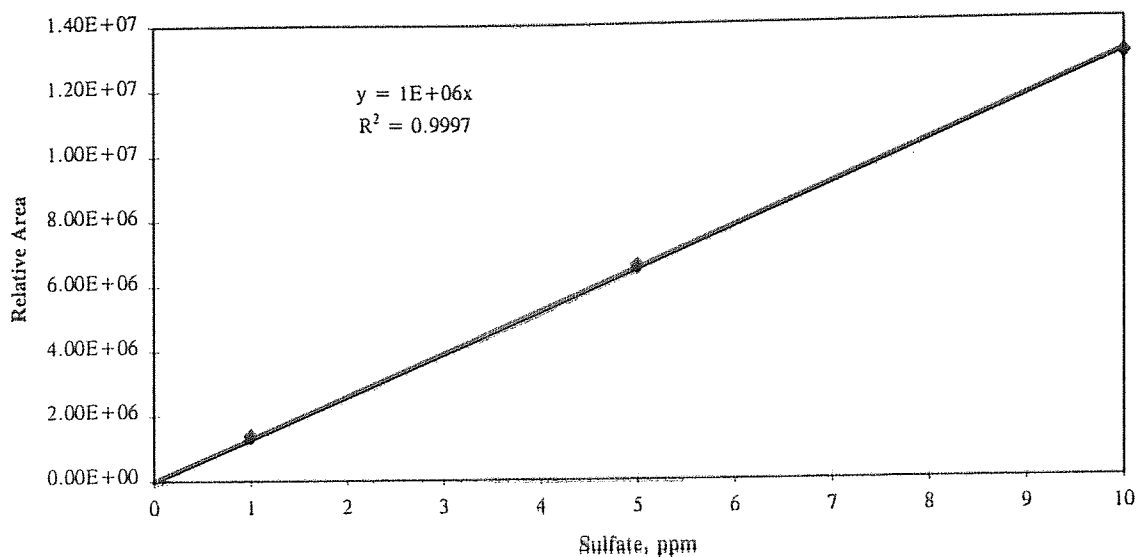


Figure 3.4 Calibration Curve for Sulfate (Conductivity Detector)

3.5.2 Gas Chromatography-Flame Ionization Detection Analysis of Tert-Butanol and Tert-Butyl Nitrite.

A Hewlet Packard model 5890 series II gas chromatograph with a flame ionization detector (FID) was used for the quantitative determination of tert-butanol and tert-butyl nitrite in the scrubbing solutions. The column used for the gas chromatograph (GC) was a 30 m x 0.32 mm ID x 0.5 μ m thickness RTX-200 capillary column. The samples were diluted in water to the proper concentration and injected into the GC. Below is a summary of the operating conditions for the GC-FID:

Oven Temperature	55 °C
Injection temperature	200 °C
Detector Temperature	250 °C
Split	9.4:1

Temperature program:

Initial oven Temperature	55 °C hold 10 minutes
Final oven temperature	105 °C at 25 °C/min hold 2 min

Gas flow:

Auxiliary	15.5 cm ³ /min
H ₂	29.5 cm ³ /min
Air	426 cm ³ /min
Split	18 cm ³ /min
Column flow	31.8 cm ³ /min

GC calibration for tert-butanol is given in Figure 3.6. The retention time for tert-butanol was 3.56 minutes. A qualitative analysis for tert-butyl nitrite was performed however, this compound was not detected in any of the scrubbing samples analyzed.

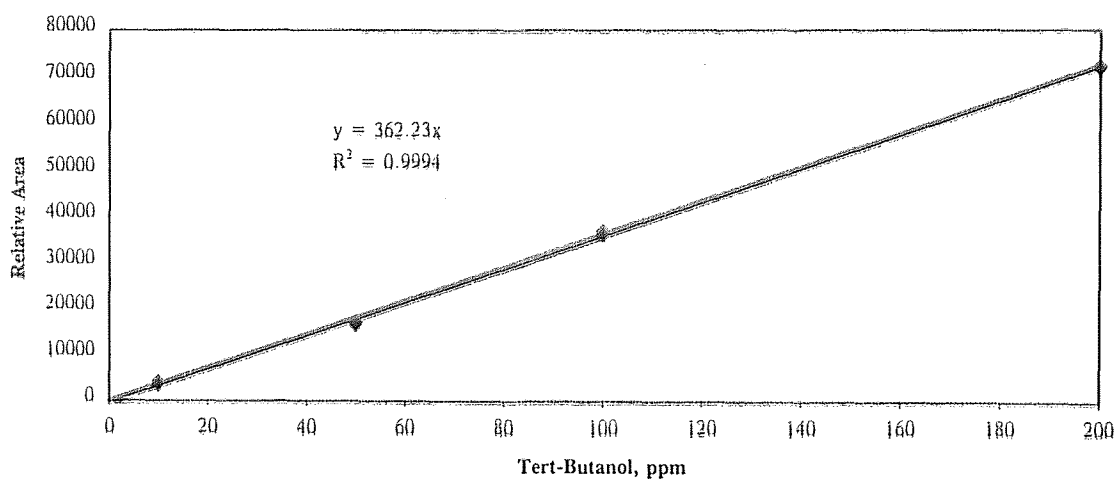


Figure 3.6 Calibration Curve for Tert-Butanol.

3.5.3 Gas Chromatography-Flame Ionization Detection Analysis of Isobutylene

A Varian 3600 GC equipped with an FID and a gas sampling port was used for the qualitative analysis of isobutylene in the effluent gas from the scrubber. The column used was an Alltech HAYASEP D 80/100 mesh, 10' x 1/8" x 0.085" SS PW. Gas flow was 30 cm³/min., H₂ and Air pressure was 40 psi @ 120 °C. The injector temperature was 76 °C, the column, 120 °C and the detector, 200 °C. Trace quantities of isobutylene were detected in the scrubber gas samples. However, it is believed that the trace quantities detected were due to thermal decomposition within the column rather than from the scrubbing reaction.

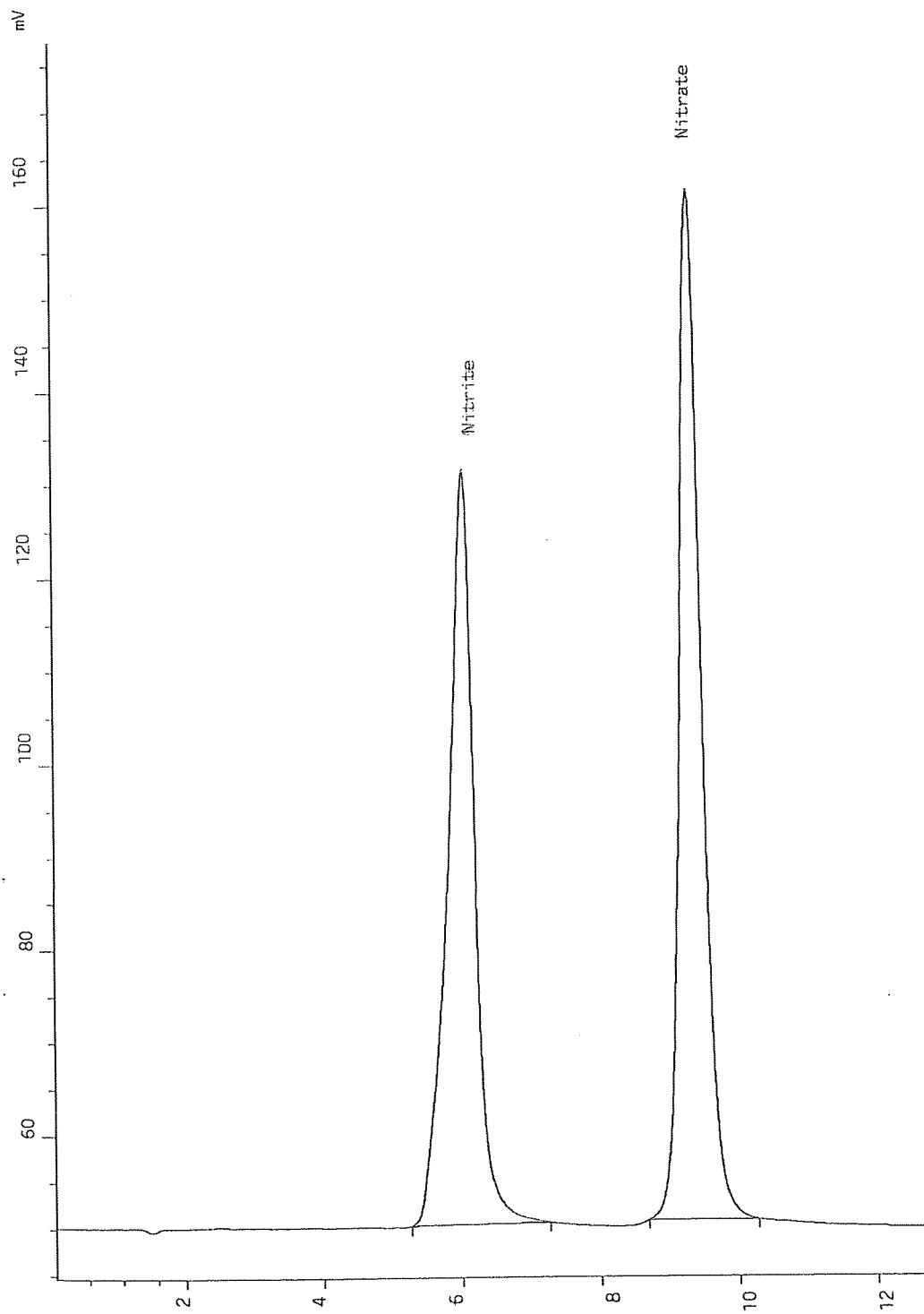


Figure 3.7 Typical IC Chromatogram from the UV Detector.

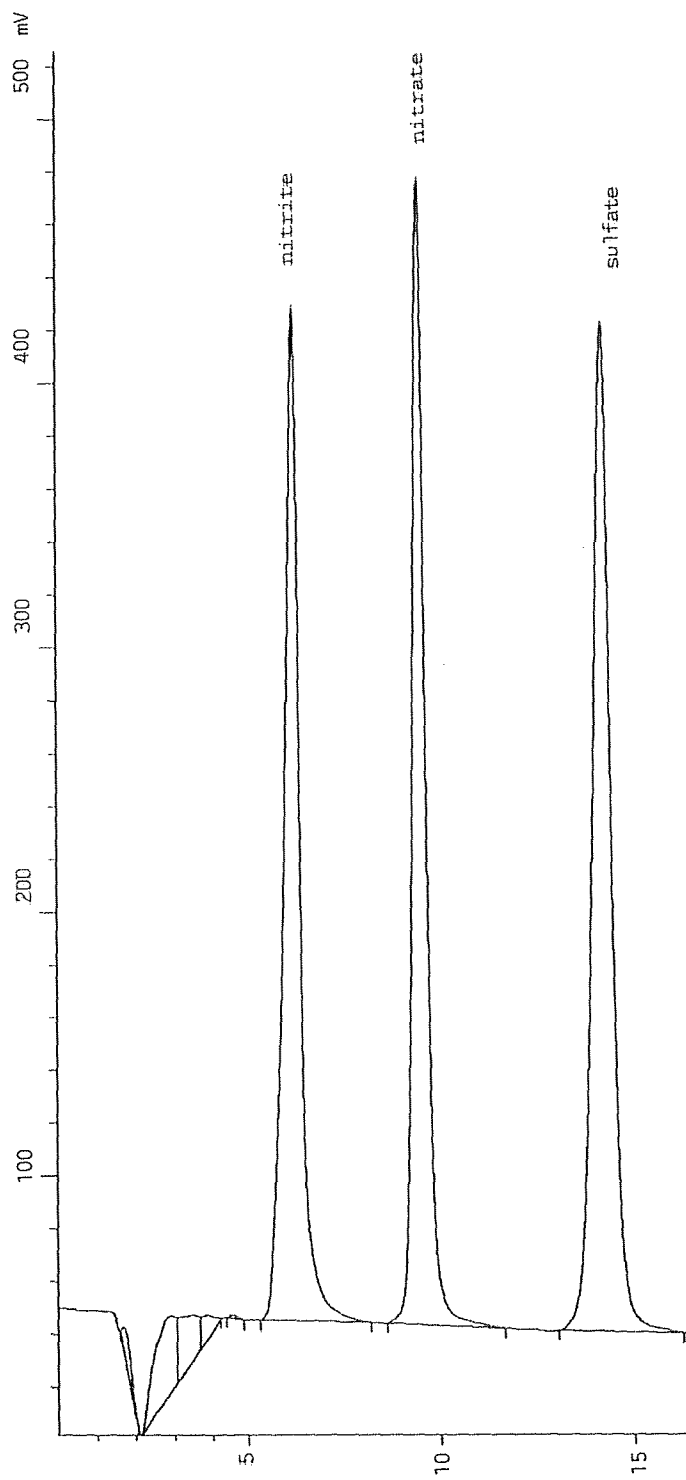


Figure 3.8 Typical IC Chromatogram from the Conductivity Detector.

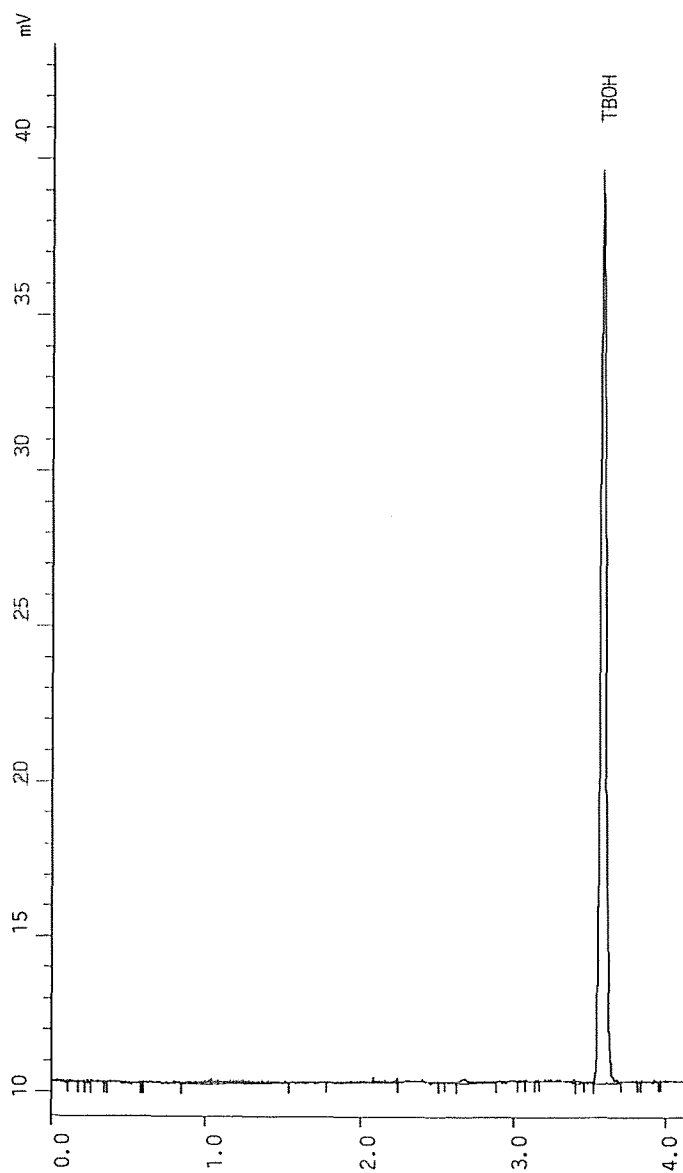


Figure 3.9 Typical Chromatogram from the FID Detector.

CHAPTER 4

RESULTS AND DISCUSSION

Aqueous solutions of TBHP were tested for their effectiveness as oxidants to remove NO from simulated flue gasses. The experiments were conducted in a semi-continuous bubbling scrubber with analyzers connected for continuous analysis of the exiting gas. The experiments were performed at different pH's, concentrations of TBHP, residence times, temperatures and concentrations of alkaline compounds.

4.1 Oxidation of NO by Tert-Butyl Hydroperoxide Solutions

Previous work similar to this study was performed by Lollertpiphop (35) who used cumene hydroperoxide (CHP) and was able to achieve 92% NO removal at 94 °C, 1.531 min. residence time, 0.12 M CHP, and 0.1 M potassium hydroxide. This work improved upon the previous study by examining the chemistry of a more soluble and reactive hydroperoxide and its suitability in removing both NO_x without interference from SO_x.

4.1.1 Effect of Tert-Butyl Hydroperoxide and NaOH Concentrations on NO Removal

Alkyl hydroperoxides are stronger acids than their corresponding alcohols. When TBHP is dissolved in alkali solutions, the salt of TBHP is formed (36)



This is useful as most scrubbing systems operate using alkali to absorb SO₂. This study is intended to demonstrate that adding TBHP will allow for control of NO in the same

scrubber being used for SO_x control. To study the effect of increasing alkali concentration on the removal of NO by TBHP, 1 dm³ of 0.2 M solutions of TBHP were prepared with varying molar concentrations of alkali. The pH was taken and recorded and the solution was placed in the scrubbing apparatus. Simulated flue gas containing 1860 ppm NO (balance nitrogen) was bubbled through the solution at 1 dm³ per minute as the solution was being heated. Readings from the NO analyzer were taken every 30 seconds until the NO conversion reached 100%. The results of these experiments are given in Figure 4.1.

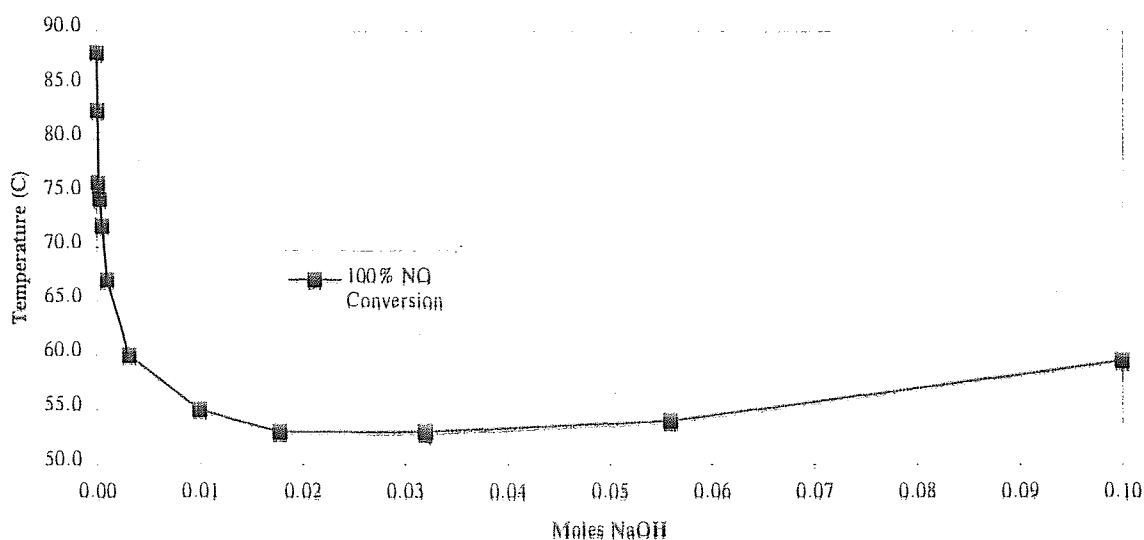


Figure 4.1 Effect of NaOH Concentration on NO Removal with 0.2 M TBHP and 1 min. Residence Time.

The results of these experiments indicate that 100% NO removal will occur at progressively lower temperatures as the concentration of the alkali increases until the ratio approaches a ratio of 1 part TBHP to 0.25 parts alkali where the temperature begins to increase. This trend continues until the concentration of the alkali approaches equimolar concentration with TBHP and the rate at which temperature increases begins to

level off (See figure 4.2). These observations can be explained in the following way. It has been reported by Kharasch, et al., (37) that TBHP is normally stable to alkali. However, the stability of TBHP is decreases under certain conditions (heat and/or light) when the concentration ratio of TBHP and its alkali salt approach 1:1 (37). This would explain the reduction in temperature for 100% removal of NO observed as the alkali concentration increased from 0.000032 to 0.02 M. However as the alkali concentration approaches or exceeds equimolar concentration with TBHP, the temperature for 100% NO removal begins to increase. This observation can be explained by the greater stability of the TBHP salt formed when excess alkali is present (37). Figure 4.2 shows the temperature curve for 100% NO removal when the molar ratio of NaOH and TBHP concentration intersect at 0.2 M.

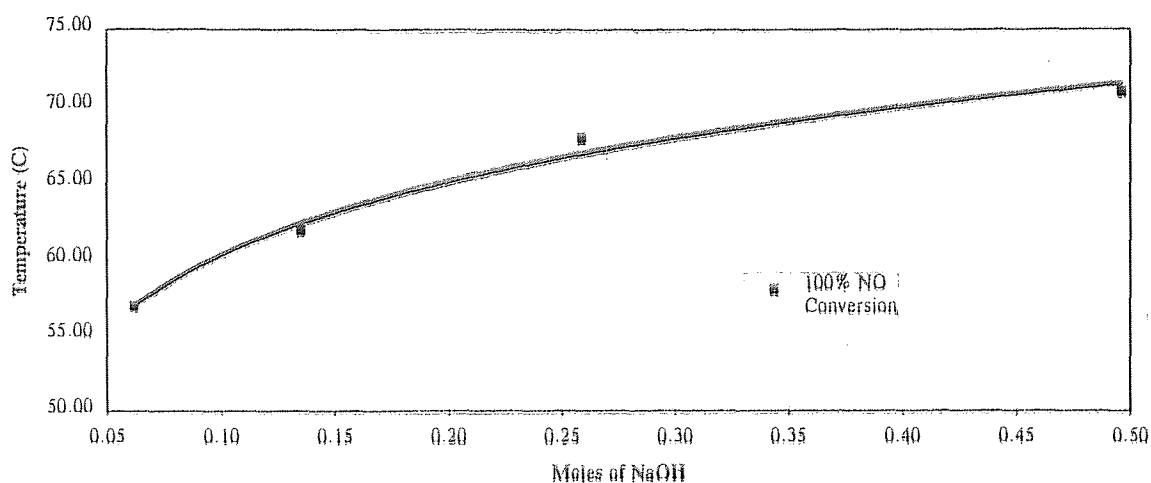


Figure 4.2 Effect of the Molar Ratio of NaOH to TBHP on NO Removal as the Concentration of NaOH goes to Excess at 0.2 M.

The data indicate that as the concentration of NaOH exceeds that of tert-butanol the salt of TBHP is formed and that salt is more stable than the hydroperoxide. These

results correspond to those reported by Swern (36) and Kharasch, et al., (37) for related hydroperoxides. The data for Figure 4.2 are given in Table 4.1 below.

Table 4.1 Effect of the Molar Ratio Between NaOH and TBHP on NO Removal.

MOLES TBHP	MOLES NaOH	NaOH/TBHP RATIO	TEMPERATURE °C
0.2	0.056	0.28:1	54.0
0.2	0.062	0.50:1	59.5
0.2	0.135	0.71:1	62.0
0.2	0.259	1.30:1	68.0
0.2	0.496	2.50:1	71.0

4.1.2 Effect of the Source of Alkali on TBHP Oxidation of NO

A number of experiments were performed to test any potential effects different alkali compounds may have in relation to TBHP and its oxidizing NO. A number of 1 dm³ solutions containing 0.2 M TBHP and equivalent amounts of either NaOH or KOH were placed in the scrubbing apparatus. Calcium oxide was tested only at saturation due to its low solubility. As each solution was heated, 1860 ppm NO in nitrogen was bubbled through and the NO escaping was recorded from the NO_x Analyzer every 30 seconds. The temperature at which 100% NO removal was observed was then recorded. Figure 4.3 shows the results of this study and indicate that the source of the alkali has no significance in relation to the oxidation of NO by TBHP. It could also be said in light of the previous section, that the salt of TBHP is equally effective in oxidizing NO regardless of the cation associated with it.

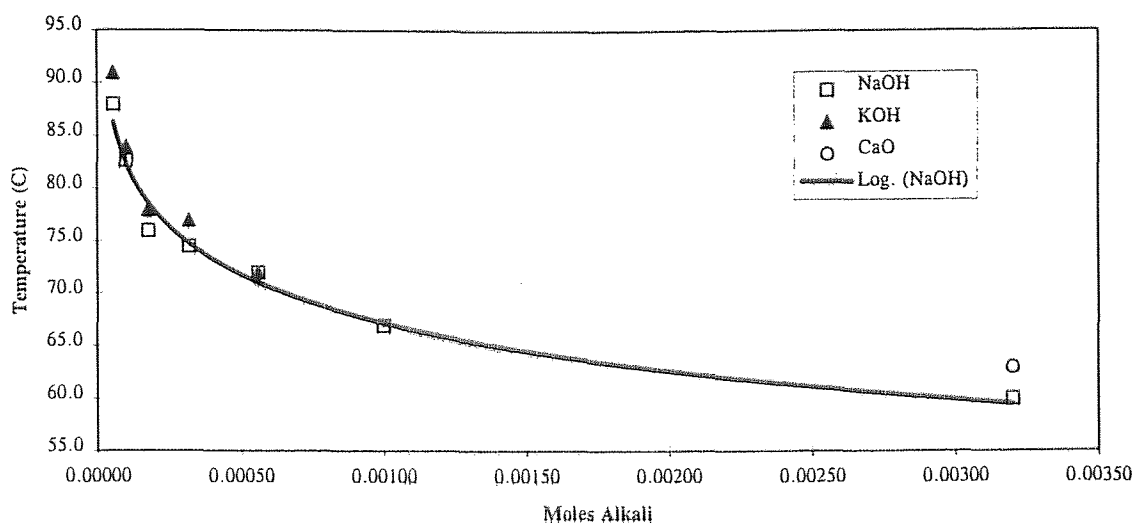


Figure 4.3 The Test of Several Alkali Compounds on the Oxidation of NO by TBHP.

4.1.3 Effect of NO Residence Time on NO Removal

Several experiments were carried out to test the oxidation of NO as a function of residence time. These experiments were carried out in solutions of 0.2 M TBHP at different NaOH concentrations while 1100 ppm NO in nitrogen was bubbled through. The temperature of the solution was raised until 100% NO removal was observed. The NO residence times for these experiments were 1.0 and 1.5 minutes.

The data for this study is given in Table 4.2. The results are shown in Figure 4.4 and indicate that higher residence times will result in complete NO oxidation at significantly lower temperatures.

Table 4.2 Effect of Residence Time on the Temperature for Complete NO Oxidation.

MOLES NaOH 1 dm ³	MOLES TBHP 1 dm ³	1.5 MINUTE RESIDENCE °C	1.0 MINUTE RESIDENCE °C
0.010	0.2	46.0	55.0
0.018	0.2	44.0	53.0
0.032	0.2	44.0	53.0

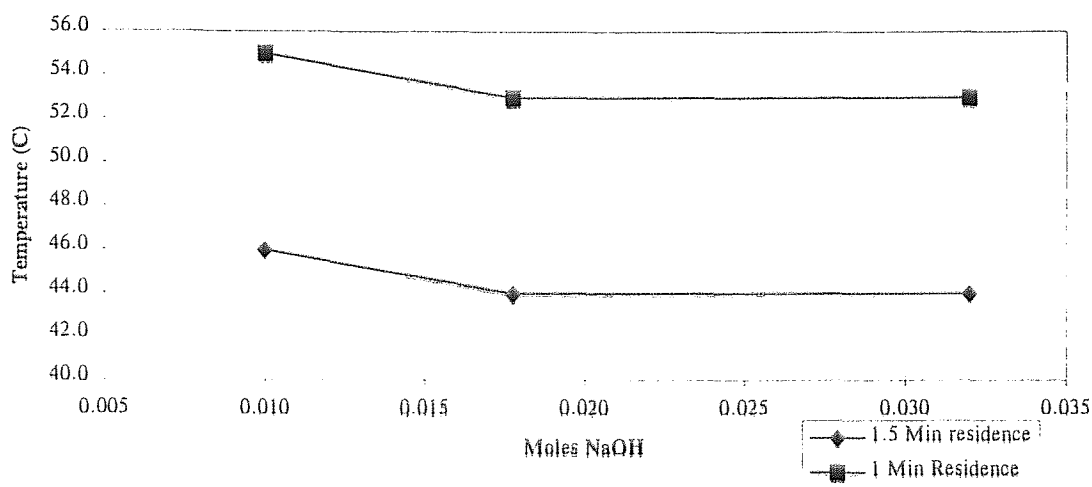


Figure 4.4 Effect of Residence Time on the Temperature for Complete NO Oxidation.

4.1.4 The Effect of TBHP Concentration on NO Oxidation

Experiments were conducted to determine the effect that increasing the concentration of TBHP would have on oxidizing NO. Solutions were prepared at 0.10 M (pH 13) and 0.018 M NaOH (pH 12.25) with 0.5, 0.9, 0.20 and 0.28 M TBHP. These solutions were placed in the scrubber and heated while 1100 ppm NO in nitrogen was bubbled through the column. The data revealed a significant relationship between TBHP concentration and the minimum temperature for complete NO oxidation. The data are shown in Figure 4.5.

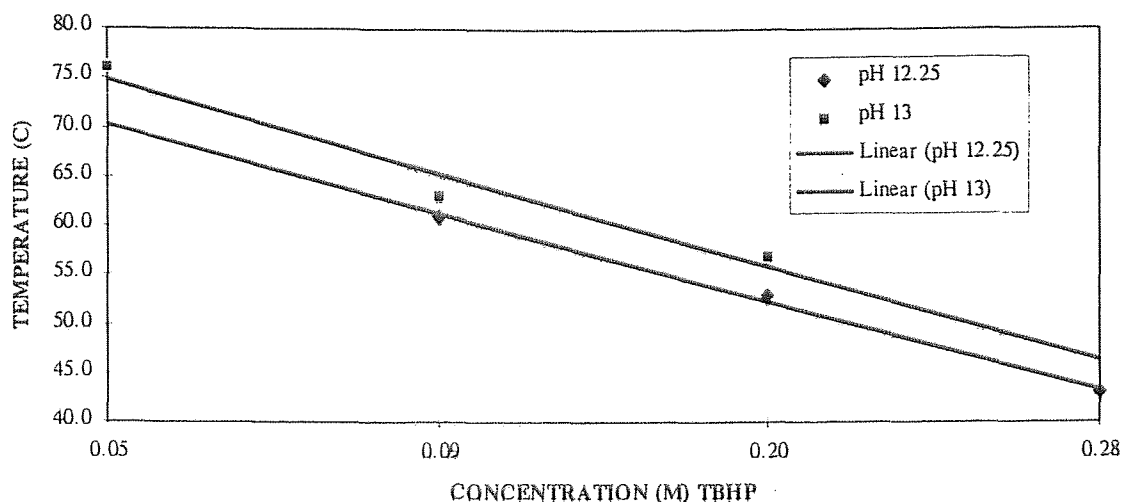


Figure 4.5 Effect of TBHP Concentration on NO Oxidation.

4.1.5 Thermal Degradation of TBHP and Sulfur/Sulfite Reaction

Thermal degradation: A series of experiments were performed to determine the rate of thermal degradation of TBHP over a range of temperatures and NaOH concentrations.

The experiments were performed with 1 dm³ of 0.10 M TBHP dissolved in alkali solutions. The solutions were heated to temperature while being purged with nitrogen. The data show that thermal degradation only occurs at temperatures above ambient regardless of alkali strength or source. A significant increase in thermal stability was noticed when the molar ratio of TBHP to NaOH was one to one versus three to one. It was observed that with a 1:1 ratio of TBHP to NaOH, TBHP was thermally stable up to 70 °C whereas at 3:1 thermal degradation was observed at 50 °C. This is not surprising since previous data had already indicated that solutions where TBHP is a salt are more stable.

A series of experiments were performed at 65 °C at different ratios of TBHP to NaOH to determine the effect increasing alkali content would have on the thermal degradation rate constant and half life. All solutions employed were 1 dm³ of 0.1 M TBHP and from 0.003 to 0.2 M NaOH. The solutions were analyzed for pH, placed into the scrubbing equipment, heated to experimental temperature and monitored for one hour. The concentration of TBHP was determined at the beginning of and after the hour. The results of the study are given on Table 4.3. An experiment using Ca(OH)₂ was also performed and the data are also given on Table 4.3.

Table 4.3 Rate Constants and Half Lives of TBHP/NaOH Solutions at 65 °C.

RATIO TBHP/NaOH	65 °C	
	k	t ½ min
0.5 to 1	-	-
1 to 1	-	-
3 to 1	0.0020563	337.01
10 to 1	0.0020563	337.01
30 to 1	0.0021167	327.40
TBHP/Ca(OH) ₂		
15 to 1	0.0030983	223.67

A second experiment tested TBHP stability at room temperature in solutions with LiOH, NaOH, KOH, Mg(OH)₂, and Ca(OH)₂ as the alkali material. A 0.1 M solution of TBHP was mixed with no alkali and divided into five 100 cm³ portions and sufficient alkali added to each portion to increase the pH to around 11.75 (except. Mg(OH)₂ which is less soluble). The remainder received no alkali and served as a control. The result of the study was that there was no thermal decomposition at ambient conditions after 48 hours for any of the samples.

Sulfur/Sulfate reaction: A second series of experiments were performed using identical experimental conditions to the thermal decomposition study above except that nitrogen containing 4934 ppm SO_2 was bubbled through the scrubber for one hour. It was discovered very quickly that the degradation of TBHP significantly increased with the introduction of SO_2 . It was observed that thermally stable solutions of 1:1 TBHP to NaOH exhibited half lives of between 224 and 337 minutes over the temperature range of 40 to 70°C. The wide variation being due to the low sensitivity of the iodometric method. Similar results were observed for all solutions tested. It was not immediately clear if the SO_2 itself was responsible for the decomposition or SO_3^- . Swern (36) made reference to a paper by Criegee, et. al., (38) who had developed a method for the determination of hydroperoxides using sodium sulfite. A simple test was devised to test the possibility that sulfite was reducing the peroxide. A sample of fresh scrubbing solution containing 0.1 M TBHP, as determined by iodometry, was taken and the total moles of oxidant in the sample was calculated and recorded. A portion of sodium sulfite equal to one half the total moles of TBHP present in the scrubbing solution was weighed and added to the solution and thoroughly mixed. After five minutes passed a sample was taken and analyzed by iodometry. The reduction in total moles of TBHP in the solution was found to be equal to the total moles of sodium sulfite added. It was then decided to try using calcium hydroxide to reduce the solubility of the sulfite with the hope of reducing sulfur reaction. This has an added advantage of being similar to scrubbing systems currently used by industry . It was found that at 65 °C the calcium hydroxide solution had a half life (237 minutes) while oxidizing SO_2 . This was similar to the half

life observed for calcium hydroxide solutions during thermal decomposition (223 minutes) under the same conditions. It seems possible that the sulfur reaction problem has been solved by reducing its solubility in aqueous alkaline solutions.

4.1.6 Material Balance and Products Analysis

All reactants and products from the reaction were determined qualitatively and quantitatively. This was done to obtain a complete material balance to account for nitrogen, carbon, and sulfur. The nitrogen balance equates the nitrogen from the NO to nitrite and nitrate products in the scrubbing solution. The carbon balance equates the TBHP and trace tert-butanol in the reactant solution with the end product, tert-butanol. The sulfur balance equates the sulfur dioxide going in to the sulfate found in the scrubbing solution.

Ion chromatography (IC) was used to determine the concentration of the inorganic products in the scrubbing solution while a NO_x analyzer was used to determine the presence of any unreacted NO. Calibration curves for nitrite, nitrate, and sulfate are given in Figures 3.2, 3.4, and 3.5 respectively. A GC-FID was employed to quantitatively determine the concentration of tert-butanol in the scrubbing solution before and after scrubbing as well as in the vapor collection system.

The material balance for nitrogen and carbon was performed at optimal operating conditions as determined from previous results. The experiment was run until breakthrough. See Figure 4.6.

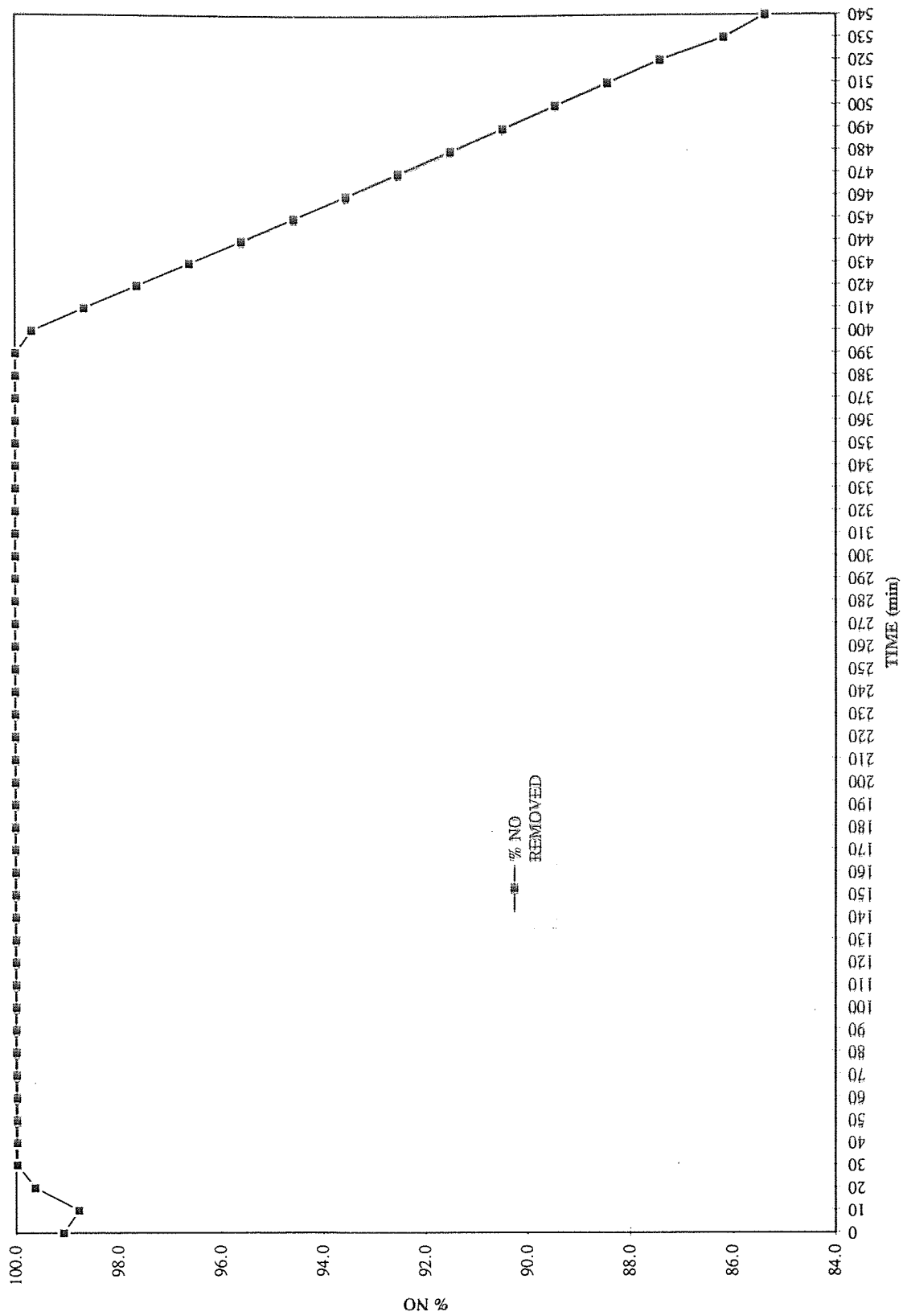


Figure 4.6 Graph of Breakthrough Experiment from 0 to 537 Minutes.

The conditions selected for this experiment are outlined below:

Scrubbing solution: 1.5 dm³ of 0.124 M TBHP in 0.1 M NaOH

Flue gas composition: 1100 ppm NO, balance N₂

Flue gas flow rate: 1 dm³/min.

Scrubbing temperature: 70 °C.

Results of the nitrogen and carbon balances on the scrubbing solution are given below in Tables 4.4 and 4.5.

Table 4.4 Nitrogen Balance for TBHP Oxidation of NO in Alkaline Solution.

Source	Compound	Initial Concentration (Moles)	Final Concentration (Moles)
Gas	NO	0.0236	0.0012
Gas	NO ₂	0.0013	-
Aqueous	NO ₂ ⁻	-	0.0158
Aqueous	NO ₃ ⁻	-	0.0078
	Total	0.0249	0.0248

Table 4.5 Carbon Balance for TBHP Oxidation of NO in Alkaline Solution.

Source	Compound	Influent (Moles)	Effluent (Moles)
Reactant	TBHP	0.1240	0.1088
Product	Tert-Butanol	0.0076	0.0186
	Total	0.1316	0.1274

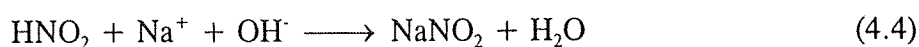
The sulfur balance was performed separately. The solution was a 0.1 molar solution of TBHP and NaOH and run at 50°C for 1 hour. The concentration of sulfur

dioxide was 4934 ppm. The concentration of TBHP was checked by iodometry before and after the experiment. The concentration of sulfate before and after the reaction was determined by IC. The results of the balance are given in Table 4.6 below:

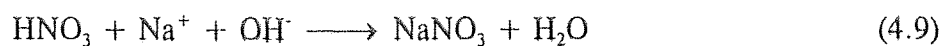
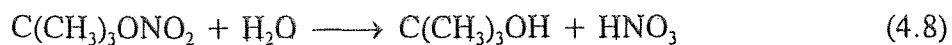
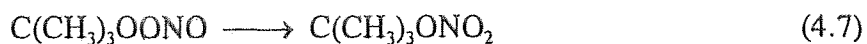
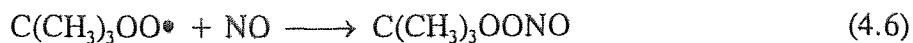
Table 4.6 Sulfur Balance in an Alkaline Solution of TBHP.

Source	Compound	Influent (Moles)	Effluent (Moles)
Reactant	SO ₂	0.022	-
Product	SO ₄ ⁻	-	0.020
	Total	0.022	0.020

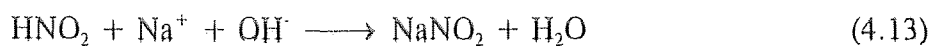
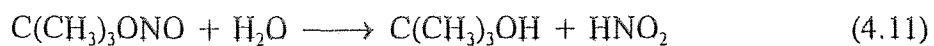
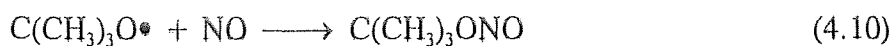
According to the analytical results of the material balance, the only end products that are produced by the oxidation of NO by TBHP are tert-butanol, and inorganic nitrite, and nitrate. It can be inferred that tert-butyl nitrite as well as tert-butyl nitrate is a short lived product of this reaction by the presence of nitrite and nitrate in the cold trap along with carryover of TBHP and tert-butanol. Neither tert-butyl nitrite or tert butyl nitrate were detected experimentally. These results can be explained by the following reactions resulting from the alkali catalyzed homolytic cleavage as described by Swern (36) and the references cited therein:



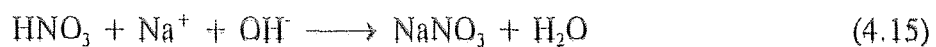
followed by:



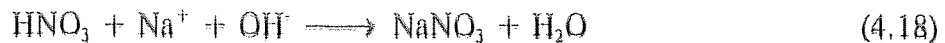
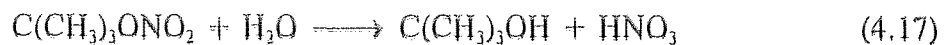
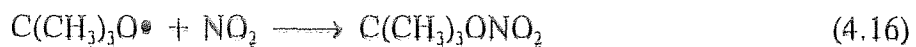
or this:



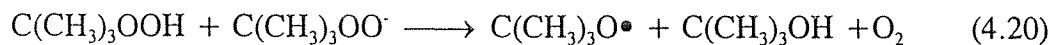
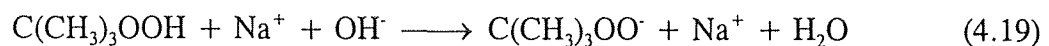
The reaction of NO_2 can be explained in the following manner:

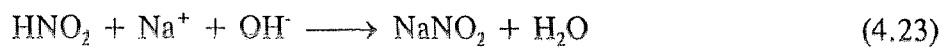
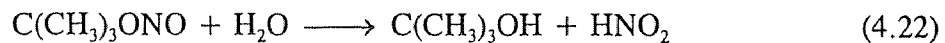
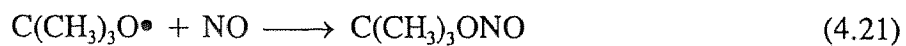


or:



The salt of TBHP may decompose and the resultant tert-butanol can react with NO as outlined below:





The reaction of NO with TBHP yields nitrite via reactions 4.3 - 4.4 and nitrate via reaction 4.5-4.9. NO₂ reacting with TBHP only yields nitrate. NO reacting with tert-butanol generated from the base catalyzed decomposition of the sodium salt of TBHP will yield nitrite.

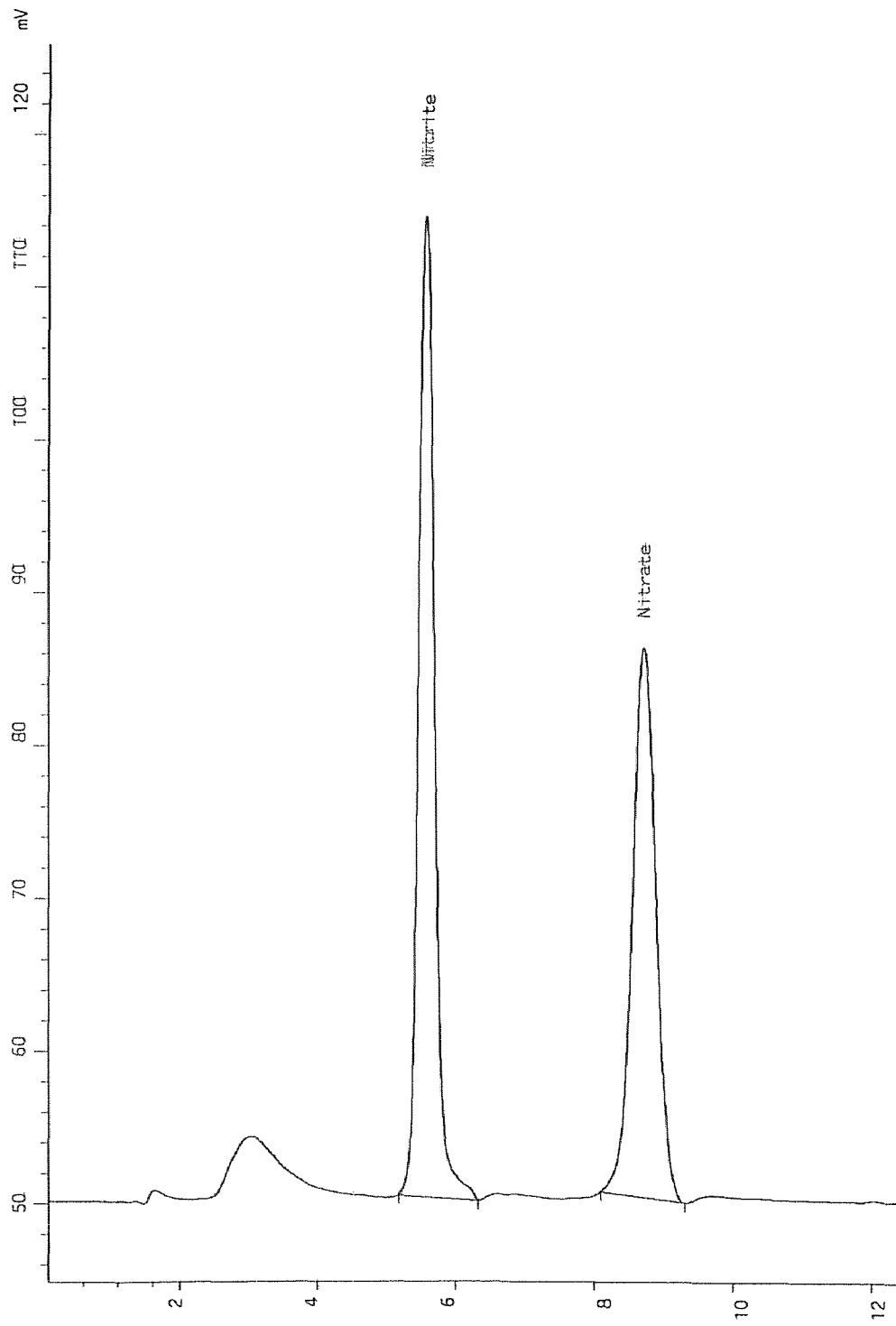


Figure 4.6 IC Chromatogram from the UV Detector on the Spent Scrubbing Solution.

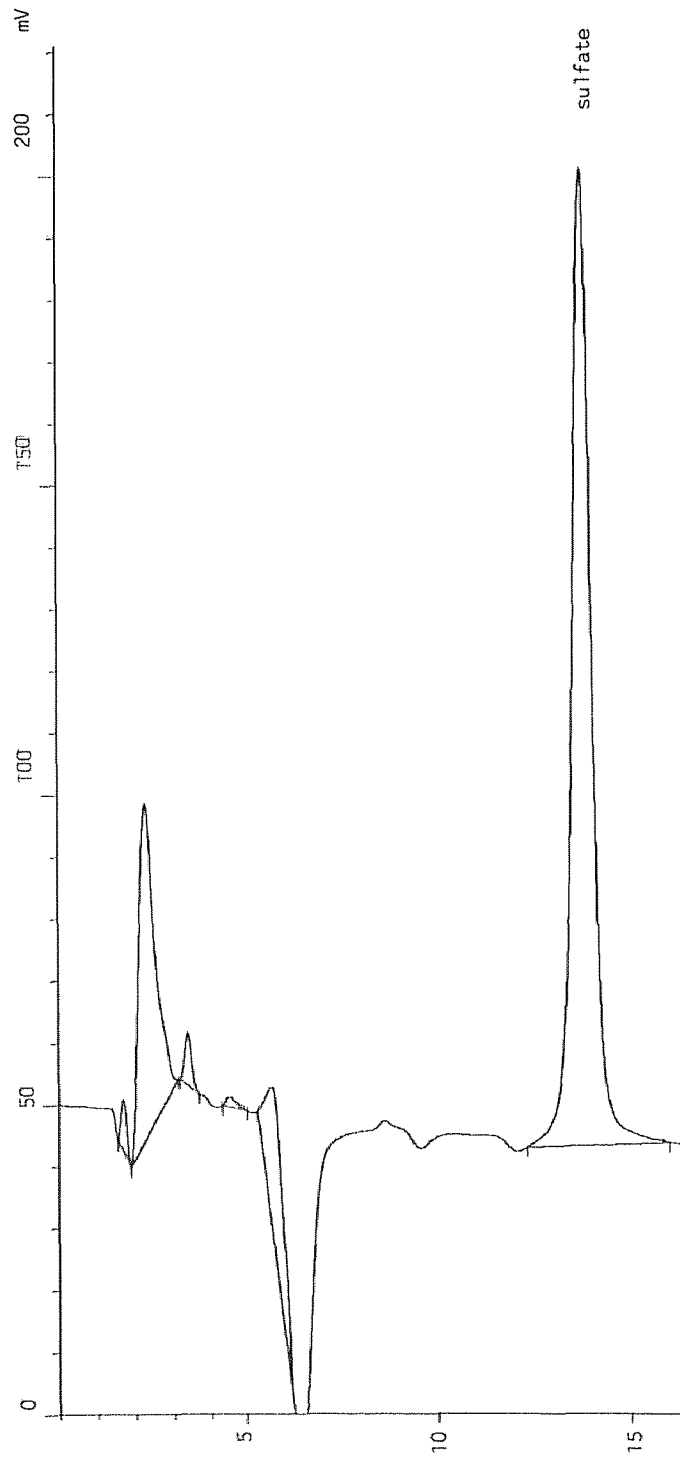


Figure 4.7 IC Chromatogram from the Conductivity Detector on the Spent Scrubbing Solution

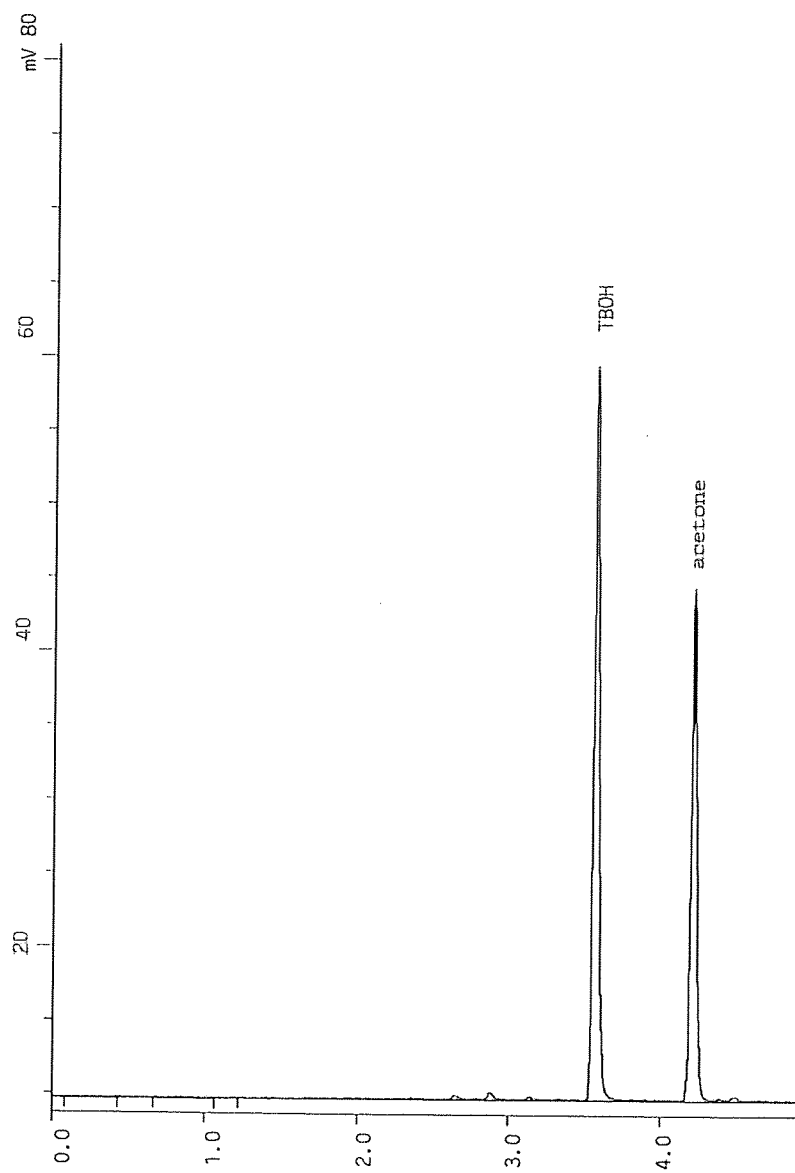


Figure 4.8 GC-FID Chromatogram of Tert-Butanol from the Spent Scrubbing Solution.

CHAPTER 5

CONCLUSIONS

Alkaline solutions of TBHP show promise of being a unique and selective choice for the oxidation and absorption of NO from flue gas. Solutions containing 0.2 M TBHP, 0.03 M NaOH (pH 12.5), and 1 minute residence time removes NO to below detectable levels at 53 °C. The source of alkali was not a significant factor. NO removal increased with increasing alkali strength, residence time and temperature up to 80 °C. Above 80 °C carryover of the reactant becomes significant. Solutions of alkali, such as NaOH and KOH, whose corresponding sulfite salts are highly soluble should be avoided when sulfur dioxide is present as the sulfite generated will react with TBHP. The best application for these NaOH and KOH solutions is where the SO₂ has already been removed from the flue gas. Solutions containing calcium hydroxide as the source of alkali (whose corresponding sulfite salt is not soluble) show little or no sulfite effect in consuming TBHP and may be a good choice for scrubbing systems where SO₂ is present. Calcium hydroxide solutions of TBHP can oxidize NO to below detectable levels with 0.2 M TBHP, 0.0056 M Ca(OH)₂ (pH 11.75), and 1 minute residence time at 63 °C.

The end products obtained from the reaction are tert-butanol, and inorganic nitrite and nitrate.

CHAPTER 6

RECOMMENDATIONS

It is recommended to continue this work to investigate the economic practicality of the TBHP alkali system in the following areas:

- Determine the scrubbing efficiency and thermal stability of TBHP in calcium hydroxide.
- Determine the kinetics and mass transfer coefficients for scale-up with calcium hydroxide solutions and sodium hydroxide solutions of TBHP.
- Obtain chemical engineering design parameters for scrubbers using TBHP and compare with designs developed for NaClO_2 scrubbers in this laboratory.

REFERENCES

1. P. M. Irving, *U. S. National Acid Precipitation Assessment Program, 1990 Integrated Assessment Report*. Washington DC: U. S. National Acid Precipitation Assessment Program, Office of the Director. pp. 1-70, November 1991.
2. H. B. Singh, "Reactive Nitrogen in the Troposphere; Chemistry and Transport of NO_x and PAN," *Envi. Sci. Tech.*, vol. 21, pp. 320-327, 1987.
3. J. S. Levine, T.R. Augustsson, I. C. Anderson, J.M. Hoell, Jr., and D. A. Brewer, "Tropospheric Sources of NO_x : Lightning and Biology," *Atmospheric Environment*, vol. 18, no. 9, p. 1797, 1984.
4. B. Bolin, and R. B. Cook, *The Major Biochemical Cycles and Their Interactions*. New York, New York: John Wiley & Sons: p. 48, 1983.
5. J. Zeldovitch, "The Oxidation of Nitrogen in Combustion and Explosives," *Acta Physicochimica USSR.*, vol. 21, p. 577, 1946.
6. H. S. Glich, J. J. Klein, and W. Squire, *J. Phys. Chem.*, vol. 27, p. 850, 1957.
7. H. Shaw, "The Effect of Water, Pressure, and Equivalence Ratio on Nitric Oxide Production in Gas Turbines," *J. of Eng. For Power, Trans. ASME*, vol. 96, p. 240, 1973.
8. B. J. Finlayson-Pitts, J. N. Pitts Jr., *Atmospheric Chemistry*. New York, New York: A. Wiley-Interscience, pp. 160-163, 419-430, 522-526, 598-600, 971-972, 1986.
9. H. Shaw, "Aqueous Solution Scrubbing for NO_x Control in Munitions Incineration," *Winter Annual ASME Meeting*, New York, Paper No. 76-WA/Fu-9, 1976.
10. H. A. Bridgeman, *Global Air Pollution: Problems for the 1990's*. London: Bellhaven Press, p. 137, 1990.

11. B. G. Isom, S. D. Dennis, and J. M. Bates, "Impact of Acid Rain and Deposition on Aquatic Biological Systems" *ASTM STP*, p. 928, 1984.
12. V. Hasselblad, D.M. Eddy, D.J. Kotchman, "Synthesis of Environmental Evidence: Nitrogen Dioxide Epidemiology Studies," *J. of the Air Pollution Control Association* vol. 42, no. 5, p. 662, May 1992.
13. D. A. Lynn, *Air Pollution Treat and Response*. Reading, MA: Addison-Wesley, pp. 104, 1976.
14. C. L. Yang, H. D. Perlmutter, and H. Shaw, "Aqueous Absorption of Nitrogen Oxides Promoted by Strong Oxidizing Agents: 1. Inorganic Oxychlorides in Nitric Acid," *Chem Eng. Com.*, vol. 143, pp. 23-39, 1995.
15. C. L. Yang, "Aqueous Absorption of NO_x Induced by Sodium Chlorite Oxidation," Master's Thesis, Department of Chemical Engineering, Chemistry, and Environmental Science, NJIT, Newark, NJ, 1990.
16. J. Makansi, "Reducing NO_x Emissions," *Power*, pp. S1-S13, Sept..1988.
17. H. Shaw, "The Effect of Water on Nitric Oxide Production in Gas Turbine Combustors," in *20th Annual Gas Turbine Conference*, ASME Paper No. 75-GT-70, 1995.
18. C. E. Jahnig and H. Shaw, "A Comparative Assessment of Flue Gas Treatment Processes: Part I - Status and Design Basis," *J. of Air Poll. Control Assoc.*, vol. 31, pp. 421-428, 1981, and *ibid*, Part II - Cost Comparison, vol. 31, pp. 596-604, 1981.
19. B. Bonn and H. Baumann, *Coal Science*. Limerick, Ireland: Elsevier, pp. 1923-1926, 1995.
20. S. Takahashi, A. Shigeru, T. Tomoyuki, A., Hidetoshi, and H. Takao, "Oxidation of Nitrogen Monoxide in a Waste Gas," *Japan Kokai Tokoy Koho*, vol. 79, p. 39095, 1979.
21. K. K. Baveja, D. Subba Rao, M. K. Sarkar, "Kinetics of Absorption of Nitric Oxide in Hydrogen Peroxide Solutions," *J. Chemical Engineering of Japan*, vol. 12, pp. 322-325, 1979.

22. E. Sada, H. Kumazawa, N. Hayakawa, I. Kudo, T. Kondo, "Absorption of NO in Aqueous Solutions of KMnO_4 " *Chemical Engineering Science*, vol. 32, pp. 1171-1175, 1977.
23. S. Uchida, T. Kobayashi, S. Kageyama, "Absorption of Nitrogen Monoxide into Aqueous $\text{KMnO}_4/\text{NaOH}$ and $\text{Na}_2\text{SO}_3/\text{FeSO}_4$ Solutions," *Ind. Eng. Chem. Process Des. Dev.*, vol. 22, pp. 323-329, 1983.
24. E. Sada, H. Kumazawa, I. Kudo, T. Kondo, "Absorption of NO in Aqueous Mixed Solutions of NaClO_2 and NaOH ," *Chemical Engineering Science*, vol. 33, pp. 315-318, 1978.
25. E. Sada, H. Kumazawa, I. Kudo, T. Kondo, "Absorption of Lean NO_x in Aqueous Mixed Solutions of NaClO_2 and NaOH ," *Ind. Eng. Chem. Process Des. Dev.*, vol. 18, no.2, pp. 275-278, 1979.
26. D. Littlejohn, S. G. Chang, "Removal of NO_x and SO_x from Flue Gas by Peracid Solutions," *Ind. Eng. Chem. Res.*, vol. 29, pp. 1420-1424, 1990.
27. T. Ishibe, T. Sato, T. Hayashi, N. Kato, T. Hata, "Absorption of Nitrogen Dioxide and Nitric Oxide by Soda Lime," *British Journal of Anaesthesia*, vol. 75, pp. 330-333, 1996.
28. J. R. Shelton, R. F. Kopczewski, "Nitric Oxide Induced Free-Radical Reactions" *Journal of Organic Chemistry*, vol. 32, pp. 2908-2910 1967.
29. D. J. Carlsson, R. Brousseau, Can Zhang, D. M. Wiles, "Polyolefin Oxidation: Quantification of Alcohol and Hydroperoxide Products by Nitric Oxide Reactions," *Polymer Degradation and Stability*, vol. 17, pp. 303-318, 1987.
30. D. J. Carlsson, R. Brousseau, Can Zhang, D. M. Wiles, "Identification of Products from Polyolefin Oxidation by Derivation Reactions," *ACS Symposium Series 364*, ch. 27, pp. 376-389, 1988.
31. H. D. Perlmutter, Huihong Ao, H. Shaw, "Absorption of NO by Strong Oxidizing Agents: Organic Tertiary Hydroperoxides in n-Hexadecane," *Environ. Sci. Technol.*, vol. 27, pp. 128-133, 1993.

32. H. Ao, "Selective Adsorption from Gas Stream with Tertiary Organic Hydroperoxide Solution," Masters Thesis, Department of Chemical Engineering, Chemistry, and Environmental Science, NJIT, Newark, NJ, 1992
33. C. D. Chen, "Nitric Oxide Absorption from Flue Gas with Cumene Hydroperoxide Solution," Master's Thesis, Department of Chemical Engineering, Chemistry, and Environmental Science, NJIT, Newark, NJ, 1993.
34. R. D. Mair and A. J. Graupner, "Determination of Organic Peroxides by Iodine Liberation Procedures," *Journal of Analytical Chemistry*, vol.36, no. 1, pp. 194-204, 1964.
35. W. Lollertpiphop, "Development of Aqueous Phase Scrubber to Oxidize and Absorb Nitric Oxide" Master's Thesis, Department of Chemical Engineering, Chemistry, and Environmental Science, NJIT, Newark, NJ, 1997.
36. D. Swern, "Organic Peroxides" New York, New York: John Wiley & Sons, Inc., vol. 1, pp. 1-40, 1971.
37. M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, "The Chemistry of Hydroperoxides. XI. Hydroperoxides as Oxidizing Agents," *J. Organic Chemistry*, vol. 17, pp. 207-220, 1952.
38. R. Criegee, H. Pilz, H. Flygare, *Berichte*, vol. 72, p. 1799, 1939.