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ABSTRACT

SELECTIVE REMOVAL OF NO_x FROM CATALYTIC CRACKING REGENERATOR EFFLUENT USING WET SCRUBBING WITH AQUEOUS SODIUM CHLORITE SOLUTIONS

**by
Pin Gu**

In most refineries, the flue gas from the regenerator in the fluid catalytic cracking (FCC) unit represents a key source of NO_x, SO_x, particulate, and CO emissions. Wet scrubbing systems have been used with great success to control particulate and SO_x emissions from typical FCC regenerator flue gas. Development of relatively inexpensive and safe additives that can be used in existing scrubbing systems to oxidize and absorb NO_x is important in order to increase the industrial options to meet the provisions of the Clean Air Act and recently proposed EPA rules. This paper explores the feasibility of removing NO_x from a typical catalytic cracking regenerator effluent gas using a wet scrubbing system with the addition of an oxidizing agent (sodium chlorite). A series of experiments were conducted in a bench-scale packed bed, a bench-scale ejector Venturi scrubber, and a pilot-scale packed bed. Various operating parameters such as gas flow rate, liquid flow rate, pH, operating temperature, gas phase compositions (NO, NO₂, SO₂, CO₂ and O₂), and oxidizing agent concentration, were studied for their effects on NO_x oxidation and absorption in the scrubbing systems. Experimental results showed that up to 90% of the NO_x and SO₂ could be simultaneously removed by the scrubbing systems. Experiments were also conducted using a feed with composition similar to that of a typical effluent from a Thermal DeNO_x pretreatment. The low concentration of NO_x after the pretreatment can still be removed using this approach.

**SELECTIVE REMOVAL OF NO_x FROM CATALYTIC CRACKING
REGENERATOR EFFLUENT USING WET SCRUBBING WITH AQUEOUS
SODIUM CHLORITE SOLUTIONS**

**by
Pin Gu**

**A Dissertation
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APPROVAL PAGE

SELECTIVE REMOVAL OF NO_x FROM CATALYTIC CRACKING REGENERATOR EFFLUENT USING WET SCRUBBING WITH AQUEOUS SODIUM CHLORITE SOLUTIONS

Pin Gu

Dr. Norman W. Loney, Dissertation Advisor
Associate Professor of Chemical Engineering, NJIT

Date

Dr. Barbara B. Kebbekus, Committee Member
Professor of Chemistry and Environmental Science, NJIT

Date

Dr. Chen-Lu Yang, Committee Member
Visiting Professor of Environmental Science and Engineering
College of Engineering
University of Massachusetts, Dartmouth

Date

Dr. Daniel J. Watts, Committee Member
Executive Director of Otto H. York Center for Environmental Engineering and Science,
NJIT

Date

Dr. Laurent Simon, Committee Member
Assistant Professor of Chemical Engineering, NJIT

Date

BIOGRAPHICAL SKETCH

Author: Pin Gu
Degree: Doctor of Philosophy
Date: August 2003

Undergraduate and Graduate Education:

- Doctor of Philosophy in Environmental Science,
New Jersey Institute of Technology, Newark, NJ, 2003
- Master of Science in Environmental Science,
East China Normal University, Shanghai, P. R. China, 1998
- Bachelor of Science in Environmental Science,
East China Normal University, Shanghai, P. R. China, 1995

Major: Environmental Science

Presentations and Publications:

Pin Gu, Norman Loney, Henry Shaw, and Chen-Lu Yang,
“NO_x Removal From Catalytic Cracking Regenerator Effluent Gases in a Venturi Scrubber,”
Proceedings of the 2002 National Conference on Environmental Science and Technology, Greensboro, NC, September 2002.

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Ninth Annual UNI-TECH Conference, Newark, NJ, April 28, 2000.

Theresa J. Takacs, Robert G. Balmer, John D. Cunic, Henry Shaw, Chen-Lu Yang, and Pin Gu,
“Process for Reducing NO_x in Waste Gas Stream Using Chlorine Dioxide,”
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“Process for Reducing the Level of NO_x in Waste Gas Stream Using Sodium Chlorite,”
Filed for United States Patent, June 2002.

To my parents

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CHAPTER 1

INTRODUCTION

According to the U.S. Environmental Protection Agency ^[1], “Since 1970, EPA has tracked emissions of the six principal air pollutants - carbon monoxide, lead, nitrogen oxides, particulate matter, sulfur dioxide, and volatile organic compounds. Emissions of all of these pollutants have decreased significantly except for NO_x which has increased approximately 10 percent over this period.”

For many refineries, a fluid catalytic cracking (FCC) regenerator represents the single largest source of particulate, nitrogen oxides (NO_x) and sulfur emissions to the air. Regulatory pressure to reduce overall refinery emissions is increasing and bringing much more attention to FCC regenerators. Among all these air pollutants from FCC regenerators, NO_x is the most difficult to control and presents serious environmental and health problems. On December 6, 2000, the Texas Natural Resource Conservation Commission (TNRCC) adopted a comprehensive Attainment Demonstration Plan to bring the Houston-Galveston Area into compliance with National Ambient Air Quality Standards for ground level ozone. The TNRCC Plan calls for reducing the emissions of NO_x by 75% in the Houston-Galveston Area by November 2007 ^[2]. FCC regenerators are considered significant sources of NO_x emissions and required to gain an emission limit of 13 ppmv by 2007 ^[2]. This presents a real challenge to the refinery industry.

1.1 Nitrogen Oxides

NO_x are a mixture of gases that are composed of nitrogen and oxygen in varying amounts. The family of NO_x compounds and their properties are listed in Table 1.1.

Table 1.1 Nitrogen Oxides ^[3]

Name	Formula	Properties
nitrous oxide	N ₂ O	colorless gas, water soluble
nitric oxide	NO	colorless gas
dinitrogen dioxide	N ₂ O ₂	slightly water soluble
dinitrogen trioxide	N ₂ O ₃	black solid water soluble, decomposes in water
nitrogen dioxide	NO ₂	red-brown gas
dinitrogen tetroxide	N ₂ O ₄	very water soluble, decomposes in water
dinitrogen pentoxide	N ₂ O ₅	white solid very water soluble, decomposes in water

Two of the most toxicologically significant nitrogen oxides are nitric oxide and nitrogen dioxide; both are nonflammable and colorless to brown at room temperature. Nitric oxide is a sharp sweet-smelling gas at room temperature, whereas nitrogen dioxide has a strong, harsh odor and is a liquid at room temperature, becoming a reddish-brown gas above 70 °F. They are also the principle nitrogen oxides formed from FCC regenerator.

The major sources of NO_x are motor vehicles, electric utilities, refinery plants, and other industrial, commercial, and residential sources that burn fuels.

1.2 NO_x Formation in a FCC Regenerator

1.2.1 NO_x Formation in Combustion Processes

Nitrogen oxides formed in combustion processes are defined by the distinct mechanisms from which they have arisen. Hence they are named as thermal NO_x, fuel NO_x, and prompt NO_x.

Thermal NO_x is formed by a series of chemical reactions in which oxygen and nitrogen in the combustion air dissociate and subsequently react to form NO_x at very high temperatures. The formation of thermal NO_x is well described by the Zeldovich mechanism. The Zeldovich mechanism postulates that thermal NO_x formation increases exponentially with increases in temperature and linearly with increases in residence time [4]. Combustion at temperature well below 1,300°C (2,370°F) forms much smaller concentrations of thermal NO_x [3].

Prompt NO_x, a form of thermal NO_x, is formed from molecular nitrogen in the air combining with fuel in fuel-rich conditions. This nitrogen then oxidizes along with the fuel and becomes NO_x during combustion. Its contribution to total NO_x is normally negligible in most combustion processes [3].

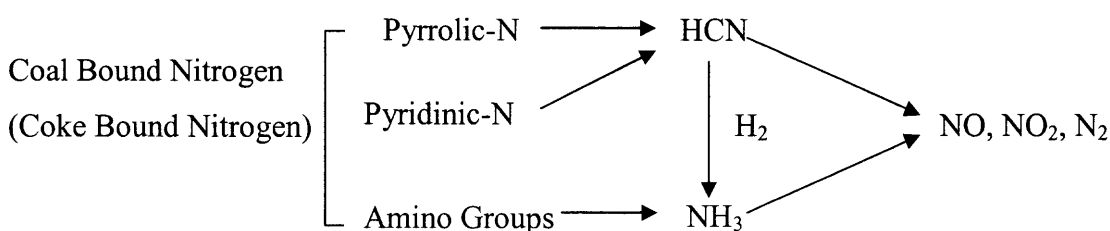
Fuel NO_x is formed from the gas phase oxidation of nitrogen compounds found in fuel. Fuel NO_x typically is the primary NO_x formed in a FCC regenerator and is further discussed below.

1.2.2 Formation of Fuel NO_x in a FCC Regenerator

The FCC unit is the part of a refinery that offers the greatest potential to increase its profitability. In this unit, large molecules are cracked, producing products such as gasoline, LPG, and diesel [5]. Cracking of heavy hydrocarbons takes place in the FCC reactor (riser). In the riser, coke is produced and deposited on the catalyst. Organic nitrogen in the feed is also deposited in the coke covering the catalyst during the cracking reaction and is especially predominant with heavy feeds, which contain higher levels of aromatic compounds and nitrogen [6]. The coked (spent) catalyst is regenerated through

combustion with an oxygen-containing gas in the FCC regenerator and NO_x may form through oxidation of nitrogen compounds in the coke ^[6, 7].

The exact chemistry on how the coke-bound nitrogen is being converted to NO_x/N₂ is not well understood. However, Zhao et al. ^[8] suggested that an analogy exists between the regeneration process (coke combustion) and fluidized bed coal combustion. It is expected that nitrogen in FCC coke would probably go through a similar transformation route as in coal combustion, which is shown below:



Zhao et al. ^[8] performed a nitrogen balance around the FCC unit, and they postulated that less than 3% of the feed nitrogen formed NO_x as a result of the oxidation of coke nitrogen, while the rest was released as N₂. The fraction of feed nitrogen that is converted to NO_x varies from 3 to 25% in commercial regenerators, depending on the design and the operating conditions. They also pointed out that the thermal oxidation of nitrogen with air makes no contribution to the NO_x in the FCC regenerator flue gas under typical regenerator conditions of 1% excess O₂ and the temperature between 730°C (1340°F) and 780°C (1430°F).

NO_x levels in the FCC regenerator flue gas typically range from 100 to 500 ppmv, in which NO is the primary component (typically 90%) with a small amount of NO₂ ^[6]. Other than NO_x, the high temperature flue gas also contains SO₂, SO₃, O₂, CO, CO₂, H₂O, and particulate ^[8], which makes it more difficult to control NO_x.

1.3 Health and Environmental Impacts of NO_x

NO_x causes a wide variety of health and environmental impacts because of various compounds and derivatives in the family of nitrogen oxides, including nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide.

1.3.1 Ground-level Ozone

Ground-level ozone is formed when NO_x and volatile organic compounds (VOCs) react in the presence of heat and sunlight. It is the primary constituent of smog. Ozone has adverse effects on the respiratory health of the very young, the elderly, and the people with lung diseases such as asthma. Ozone can be transported by wind currents and may cause health impacts far from original sources. Millions of Americans live in areas that do not meet the health standards for ozone. Other impacts from ozone include damaged vegetation and reduced crop yields ^[1].

1.3.2 Acid Precipitation

NO_x and sulfur dioxide react with other substances in the air to form acids which fall to earth as rain, fog, snow or dry particles. Some may be carried by wind for hundreds of miles. Acid precipitation damages vegetation, alters biological communities, surface waters and natural structures, and causes deterioration of cars, buildings and historical monuments ^[1].

1.3.3 Particles

NO_x reacts with ammonia, moisture, and other compounds in air to form particles that are smaller than 2.5 microns in aerodynamic diameter (PM-2.5). Epidemiological data indicate that many human health concerns, such as lung tissue damage and premature

death, are closely correlated with the amount of PM-2.5 in the air ^[3]. PM-2.5 can penetrate deeply into sensitive parts of the lungs and cause or worsen respiratory disease such as emphysema and bronchitis ^[1].

1.3.4 Visibility Impairment

Nitrate particles and nitrogen dioxide can block the transmission of light, reducing visibility in urban areas and on a regional scale in the national parks ^[1].

1.4 Regulatory Status

The 1990 Clean Air Amendments (CAAA90) made a significant departure from previous amendments in the way it began to define the problem of ground-level ozone. The CAAA90 marked the first time that the transport of ozone and its precursors, mainly NO_x, was recognized as a fundamental component of the ground-level ozone problem ^[9]. Following the course set out by the CAAA90, the U.S. Environmental Protection Agency (EPA) announced new national ambient air quality standards (NAAQS) for ground-level ozone on July 16, 1997 ^[10]. In this new standard, EPA phased out and replaced the previous 1-hour primary ozone standard (health-based) with a new 8-hour standard to protect against longer exposure periods. EPA also set the standard at 0.08 parts per million (ppm) instead of the previous 0.12 ppm and defined the new standard as a "concentration-based" form, specifically the 3-year average of the annual 4th-highest daily maximum 8-hour ozone concentrations.

In order to achieve this more stringent ambient-air ozone standard, EPA has established the NO_x State Implementation Plan (SIP) Call rule, promulgated on September 24, 1998. This rule sets summer ozone season (May 1 to September 30) NO_x

budget for states in the SIP Call region, comprising 22 eastern and Midwestern states and the District of Columbia. The goal of this rule is to reduce total emissions of NO_x by 1.2 million tons in the affected states by 2007. To meet this target, additional controls for fossil-fired units would require an overall 64% reduction capability during the summer ozone season ^[11].

EPA also authorizes each state to develop and implement plans to reach and maintain a minimum air quality standard. In Texas, this state body is the Texas Natural Resource Conservation Commission. On December 6, 2000, the TNRCC adopted the comprehensive Attainment Demonstration Plan, commonly referred to as the Smog Plan, to bring the Houston-Galveston area into compliance with one-hour National Ambient Air Quality Standards for ground level ozone. Houston-Galveston area is one of the nation's severe ozone nonattainment areas. The Smog Plan calls for reducing the emissions of NO_x by 75% in this area by 2007 ^[2]. About two-thirds, of the reductions come from industrial point sources, which result in an average 90% cut in industrial plant's emissions of NO_x by March 31, 2007 ^[2]. Refinery industry, one of the biggest contributors to NO_x emissions in this area, faces this extreme challenge to cut 90% of NO_x emissions and reach an emission standard of 13 ppmv by 2007 ^[2].

1.5 Control Technologies for FCC Regenerator

NO_x emissions from FCC regenerators can be partly controlled by combustion modification techniques, and more completely controlled by post-combustion treatment. For combustion modification techniques, BOC Gases Technology Center ^[7] claimed that FCC regenerator NO_x emissions can be reduced by 20 to 40 percent within the context of

typical commercial oxygen enrichment operation while SO_2 is largely unaffected. Grace Davison Corporation ^[8] developed a commercial DeNO_x additive with a NO reduction rate up to 50%. They also proposed some strategies on controlling NO_x through a CO combustion promoter and a countercurrent regenerator design. However, combustion modification techniques, by themselves, are insufficient to meet regulations, which then motivates the use of post-combustion treatment.

Post-combustion methods include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), and wet scrubbing ^[12, 13, 14].

1.5.1 Selective Catalytic Reduction

The SCR process consists of injecting ammonia upstream of a catalyst bed. NO_x reacts with the ammonia and is chemically reduced to molecular nitrogen and water vapor. Titanium oxide is the most commonly used SCR catalyst material. SCR can achieve up to a 94 percent NO_x reduction. However, this technology is difficult (requires very large catalyst bed capacity) and expensive to implement in retrofit application. In addition, SCR NO_x control performance is known to vary significantly with incoming NO_x concentration levels and exhaust gas flow changes associated with load following as well as ammonia distribution ^[15].

1.5.2 Selective Non-catalytic Reduction

SNCR is a cost-effective NO_x control method that can provide medium range reduction. In SNCR, ammonia or urea is injected into the flue-gas duct where the temperature favors the reaction of ammonia/urea with NO_x, typically between 900°C and 1100°C, without a catalyst. The temperature band in SNCR is important because outside of it either more

ammonia slips through or more NO_x is generated than is being chemically reduced. The difficulty of controlling the narrow temperature band is the main drawback of this method.

1.5.3 Wet Scrubbing

Wet scrubbing is a process of NO_x absorption from a flue gas into a liquid solution in a wet scrubber. Research on NO_x scrubbing processes has shown that these processes require expensive oxidation reagents and may present special disposal problems if a high concentration of oxidant is used ^[13]. Nevertheless, scrubbing promises to be competitive with other post-treatment technologies since it removes over 80% of NO_x, and in the same system can also remove other acid gases and particulate. Furthermore, since scrubbing is the primary technology used for SO₂ control, there are economies associated with scrubbing being used for other pollutants at the same facility. As an example, numerous FCC Units already have wet gas scrubbers (WGS) installed to control SO₂ and particulate. With the addition of oxidizing agents, these systems can be easily transformed to remove NO_x simultaneously.

CHAPTER 2

LITERATURE REVIEWS

Wet scrubbing has been used with great success to control particulate and SO_x emissions from FCC regenerator effluent gas. Most installations utilize caustic soda to absorb SO_x resulting in an effluent containing a soluble sodium sulfate salt. However, nitric oxide (NO), which represents 90% in the flue gas from FCC regenerator, can not be easily removed by scrubbing due to its low solubility. In order to make wet scrubbing an effective controller of NO_x from FCC regenerator, the addition of a strong oxidant is required to oxidize NO from either the gas or liquid phase. This results in the production of more soluble oxides of nitrogen, such as NO₂, N₂O₃, HNO₂, and HNO₃.

2.1 Solubility

The solubility of nitrogen containing compounds can be demonstrated by the Henry's constants as in the following relationship:

$$P_i = H_i X_i,$$

Where P_i is partial pressure of component i in the gas phase, and X_i is mole fraction of gas i in the water phase.

Table 2.1 Henry's Constants ^[18]

Gas	H (atm/mol fraction)
N ₂	86,400
NO	27,700
NO ₂	113
N ₂ O ₄	0.71
HNO ₂	0.020
HNO ₃	4.8E-6
SO ₂	44

Values of Henry's constants for some of the air pollutants are shown in Table 2.1.

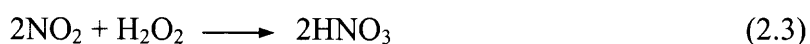
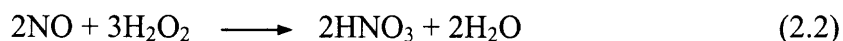
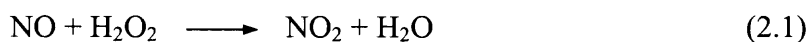
NO_2 , HNO_2 , and HNO_3 are much more soluble in water than NO from Table 2.1.

2.2 NO Absorption into Solution Accompanied by Oxidation Reaction

Because NO can not be easily converted to NO_2 , it is important to chose an oxidant that is highly reactive. This choice is particularly critical in the case of scrubbing a low NO concentration flue gas. In recent years, there have been a number of promising oxidants employed by researchers to react with NO . Some of them are: hydrogen peroxide (H_2O_2), potassium permanganate, sodium chlorite (NaClO_2), peroxyacids and organic peroxides.

2.2.1 Hydrogen Peroxide

Experiments using H_2O_2 to oxidize NO were conducted by several researchers. Kasper, et al. reported NO conversions of 97% and 75% at $\text{H}_2\text{O}_2/\text{NO}$ mole ratios of 2.6 and 1.6 respectively in a gas phase reaction at 500°C in a laboratory quartz tube reactor ^[18]. Baveja et al. and Robinson studied the reaction kinetics of liquid phase NO oxidation in H_2O_2 solutions ^[19]. They reported that the rate of reaction for both NO and H_2O_2 to be first order. Their reaction involves the following steps:

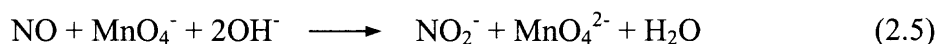


2.2.2 Potassium Permanganate/Sodium Hydroxide

Sada et al. ^[20], and Uchida et al. ^[15] conducted experiments using aqueous solutions of KMnO_4 with and without NaOH . The reaction was reported to be first order for both reactants. The reported chemical reaction for the neutral solution is:



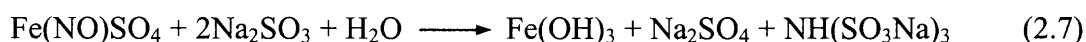
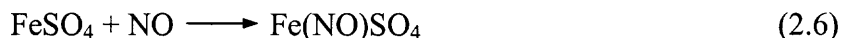
The reported chemical reaction for the $\text{KMnO}_4/\text{NaOH}$ system is:



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.

2.2.3 Sodium Sulfite/Ferric Sulfate

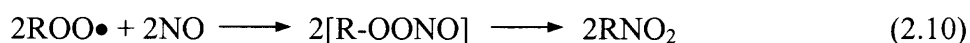
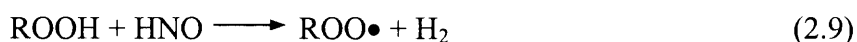
Uchida et al. studied absorption of NO with $\text{Na}_2\text{SO}_3/\text{FeSO}_4$ solutions ^[21]. They reported that NO absorption increases with the increase of Na_2SO_3 concentration up to a maximum concentration of $1 \times 10^{-4} \text{ gmol/m}^3$ with a constant FeSO_4 concentration. Above this 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:



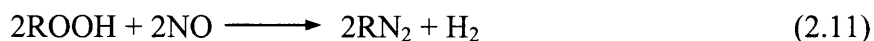
2.2.4 Organic Hydroperoxide

Permuter ^[22] and Huihong Ao ^[23] studied the selective removal of NO from gas streams using 3,6-dimethy-3-octyl hydroperoxide, p-menthanyl hydroperoxide, pinanyl hydroperoxide and cumene hydroperoxide solutions in n-hexadecane. Cumene

hydroperoxide was determined to be the most efficient in oxidizing NO among these organic hydroperoxides. In the evaluated system, NO reacted with the hydroperoxides to form alkyl nitrates. They 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:



Edwards, Shaw, and Perlmutter^[12] studied selective removal of NO with alkaline solutions of tert-butyl hydroperoxide (TBHP) in a bubbling scrubber. Their experiments showed that solutions containing 0.2 M TBHP, 0.03 M NaOH (pH 12.5), and 1 minute NO residence time could remove NO to below detectable levels at 53°C. NO removal increased with increasing ratio of alkali to TBHP, residence time, and temperature up to 80°C. Above 80°C, vaporization and loss of the reactant become significant.

2.2.5 Chlorine Dioxide

The overall reaction of NO with chlorine dioxide (ClO₂) is as follows:



Two Japanese patents confirmed this process with flue gas flow rates of 300 m³/hr and 70,000 m³/hr^[24, 25]. The conversion of NO in both cases was about 90%. The produced NO₂ was suggested to be scrubbed with alkaline solutions.

2.2.6 Chlorine

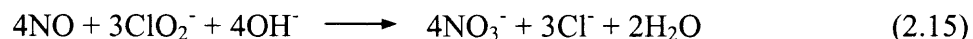
The chlorine injection for NO removal from flue gas was patented by Dow Company ^[26]. This process consists of injection of Cl₂ into NO laden gas stream followed by rigorous scrubbing using an acidic aqueous solution. The reaction is proposed as:



Yang ^[13] studied the absorption of NO by Cl₂ in bubbling column. He did not report any effect of pH on NO conversion. More than 50% of NO was converted to NO₂ in the bubbling system.

2.2.7 Sodium Chlorite

Sada et al. ^[27, 28] first studied the absorption of NO in aqueous NaClO₂ solutions. He proposed the reaction of NO with NaClO₂ in the presence of NaOH as below:



The specific rate of absorption was given as below:

$$R_A = P_{\text{NO}} H_{\text{NO}} \left(\frac{2}{3} K_{\text{NO}} D_{\text{NO}} [\text{NO}] [\text{ClO}_2^-] \right)^{0.5} \quad (2.16)$$

Where K_{NO} = rate constant

D_{NO} = diffusivity of NO in water

P_{NO} = partial pressure of NO

K_{NO} is given by the following equation:

$$K_{\text{NO}} = k_0 \exp^{-3.73[\text{NaOH}]} \quad (2.17)$$

The above equation shows that the value of K_{NO} decreases with an increase in the concentration of NaOH.

Yang and Shaw studied the absorption of NO by aqueous solutions of NaClO₂ in bench scale bubbling column, packed bed scrubber, and spray chamber scrubber [13, 17, 30]. Up to 95% of NO_x removal was obtained in the packed bed system. For a combined NO_x/SO₂ scrubbing, HNO₃, H₂SO₄ and NaCl are the end products in the spent scrubbing solutions. NaOH inhibits the oxidation of NO but enhances the utilization of NaClO₂ for NO removal to more than 100% partly due to the NO + NO₂ reaction. They suggested a low pressure drop spray chamber scrubber to be used as a prescrubber to convert 50% of NO to NO₂, and the mixture of equal molar NO/NO₂ flue can be absorbed into an alkaline solution without an oxidizing agent.

CHAPTER 3

FEASIBILITY STUDY

The feasibility of controlling NO_x from FCC regenerator effluent gas by wet scrubbing has been advanced in our laboratory. Aqueous solutions of tertiary butyl hydroperoxide, sodium hypochlorite (NaClO), chlorine dioxide, and sodium chlorite, were tested in bench-scale equipment to determine their feasibility as FCC regenerator NO_x controllers. Below is a brief description of the bench-scale study and results.

3.1 Experimental

The experimental scrubbing apparatus consists of a flue gas blending system, a gas scrubber and an analytical train. Figure 3.1 presents the schematic of the experimental system. The blending system is capable of producing a mixture of nitrogen, oxygen, nitric oxide, nitrogen dioxide, sulfur dioxide and carbon dioxide to simulate a FCC regenerator flue gas. A bench-scale packed bed is used as the scrubber. The effluent gas was continuously measured by a HORIBA Model CLA-220 chemiluminescent NO/NO_x analyzer, Rosemount Model 890 UV SO₂ analyzer, and Nicolet 520 FTIR.

3.1.1 Reagents

The individual gases were obtained from Matheson Gas Co. at specified component composition. All gases were used without further purification.

Tertiary butyl hydroperoxide was obtained in commercial grade (70 wt% in water) from Aldrich Chemical Company, Inc. Chlorox bleach (5.25 wt% NaClO) was

used to prepare sodium hypochlorite scrubbing solutions. Sodium chlorite flake was obtained from Alfa Aesar Inc. with a purity of 80%.

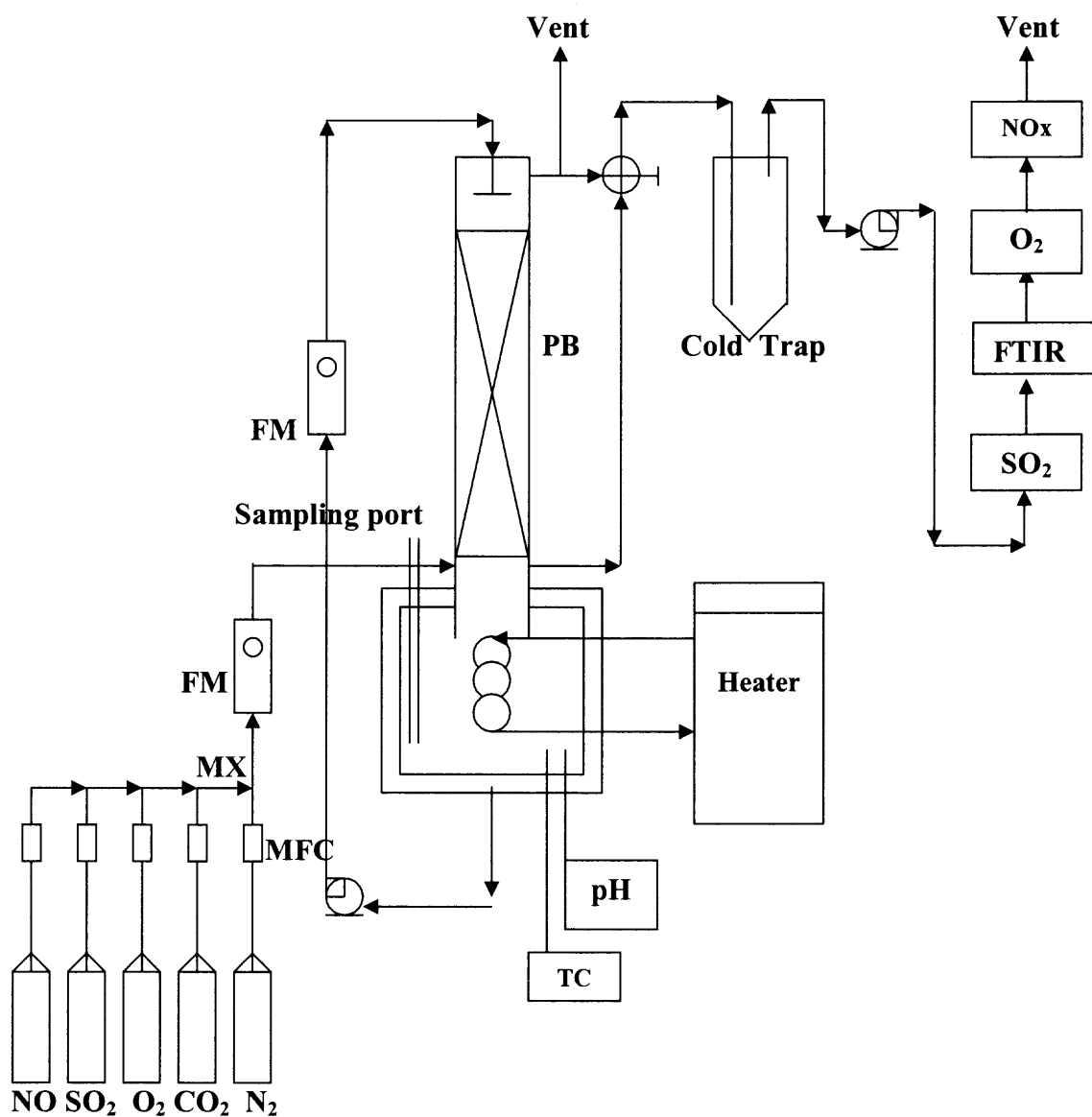


Figure 3.1 Schematic Diagram of Bench-scale Packed Bed Scrubbing System.

Chlorine dioxide solutions were prepared daily by acidification of NaClO_2 with subsequent scrubbing of ClO_2 through a NaClO_2 salt tower to remove any Cl_2 formed in this process. TBHP, NaClO , ClO_2 , and NaClO_2 stock solutions were standardized by iodometric titration. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and potassium phosphate, monobasic (KH_2PO_4), used for the preparation of pH buffer solutions, were obtained from Aldrich Chemical Company, Inc. All buffer solutions of different pHs were prepared according to the standard methods ^[24].

3.1.2 Flue Gas Blending System

The flue gas blending system was designed to simulate a FCC regenerator flue gas from high-pressure cylinders. Each component gas was delivered through ¼ inch Teflon tubing through a Porter Model PCIM4 mass flow controller (MFC), mixing with nitrogen balance gas delivered through 3/8 inch PVC tubing. The gas mixture was then delivered through ½ inch PVC tubing to the packed bed. A sufficient length of tubing (approximately 100 times the tubing diameter), from the point of introduction of the gas mixture up to the entrance of the packed bed, was used as a premixing zone. This ensured that the gas mixture entering the scrubber was of uniform composition. The total flow rate from the blending system ranged from 7 to 73 liters per minute.

3.1.3 Scrubbing Vessels

The flue gas scrubber is a 7.6 cm (3 inch) in diameter by 0.91 m (36 inch) in height bench-scale plastic column packed with 1.27 cm (1/2 inch) plastic Raschig Rings. The packing height is 25 inch. The volume of the liquid container of the system is 7 liters.

The solution in the container can be heated up to 100°C by a heating coil connected with a RTE 110 water bath heater.

Seven liters of scrubbing solution was used to run these experiments in a semi-batch mode with continuous flue gas injection. The exiting gas was carried to the analyzers from the top of the column after moisture condensation at 0°C. A sampling port on the solution tank was used to collect liquid samples for analysis.

3.1.4 Analysis

The inlet and outlet gas compositions were continuously analyzed by NO/NO_x analyzer, SO₂ analyzer and FTIR.

A HORIBA Model CLA-220 chemiluminescent NO/NO_x analyzer was used to measure the concentration of NO and NO₂. This instrument makes use of the chemiluminescent properties of the NO reaction with ozone as a measure of NO concentration. It measures NO₂ by thermally converting the NO₂ to NO at 700°C and measuring the incremental increase in concentration of NO. The sensitivity of CLA-220 is less than 1 ppmv of NO/NO_x. The instrument was calibrated with an analyzed mixture of 220 ppmv NO and 100 ppmv NO₂ in nitrogen.

SO₂ was measured continuously by a Rosemount Model 890 UV SO₂ analyzer by using its ultraviolet absorption property. The sensitivity of this instrument is less than 0.1 ppmv of SO₂. The instrument was calibrated with an analyzed mixture of 497 ppmv SO₂ in nitrogen.

A Nicolet 520 FTIR equipped with a 2 m gas cell was used to detect any N₂O that may be produced during the scrubbing process. The instrument was calibrated with certified gaseous mixtures in which helium is the balance gas. At least three different

mixtures in the range of interest are used to obtain the overall calibration curve. The FTIR was used in a scanning mode of 20 scans per sample.

3.2 Results

The results of the packed bed scrubbing experiments and the comparison between the oxidizing agents tested are given in this section. First, a model for absorption with chemical reaction in a packed bed is introduced below.

3.2.1 Model for Absorption with Chemical Reaction in a Packed Bed

The height of transfer unit (HTU) for NO_x oxidation and absorption in the packed bed is correlated to gas flow rate for evaluating the efficiencies of these oxidizing agents. The HTU are calculated from a model adopted by Yang ^[23]. The model considers a packed bed with a cross sectional area of Ω , and a differential volume of ΩdZ in a height of dZ . The change in molar flow rate F is neglected in this model, therefore the amount absorbed in section dZ is $-Fdy$, which is equal to the absorption rate times the differential volume:

$$-Fdy = K_{ga}(y-y^*)\Omega dZ \quad (3.1)$$

Where y is the mole fraction of solute in gas, y^* is the gaseous mole fraction that would be in equilibrium with aqueous mole fraction, and K_{ga} is the volumetric mass transfer coefficient.

This equation is rearranged for integration by grouping the factors F , ΩdZ , and K_{ga} with dZ .

$$\frac{K_g a \Omega}{F} \int_b^{z_t} dZ = \frac{K_g a \Omega Z_t}{F} = \int_b^a \frac{dy}{y - y^*} \quad (3.2)$$

The equation for column height Z_t can be written as follows:

$$Z_t = \left[\frac{\left(\frac{F}{\Omega} \right)}{K_g a} \right] \int_b^a \frac{dy}{y - y^*} \quad (3.3)$$

The integral in the above equation is the number of transfer units (NTU) based on the individual driving force, and the coefficient of the integral is the height of a transfer unit (HTU) based on the overall gas film coefficient.

Yang ^[23] suggested that if the reaction is essentially irreversible at absorption conditions, the equilibrium partial pressure y^* is zero, thus the NTU can be calculated just from the change in gas composition as follows:

$$NTU = \int_b^a \frac{dy}{y} = \ln \left[\frac{y_{in}}{y_{out}} \right] \quad (3.4)$$

Where y_{in} is the inlet solute gas mole fraction, and y_{out} is the outlet solute gas mole fraction.

From equation (3.4), HTU can be calculated as:

$$HTU = \frac{Z_t}{NTU} = Z_t / \ln \left[\frac{y_{in}}{y_{out}} \right] \quad (3.5)$$

HTU was used for the determination of NO_x removal efficiency with NaClO₂ in packed bed scrubbing system.

3.2.2 Comparison between the Oxidizing Agents

Figure 3.2 shows the NO_x oxidation and absorption efficiencies of all these oxidizing agents. All these experiments were conducted in the packed bed with a liquid flow rate

(LFR) of 2.4 liter/min. The temperature for all the scrubbing solutions was 60°C, and the inlet flue gases contain 350 ppmv NO_x, 500 ppmv SO₂, and 3% O₂ in N₂ balance gas.

All of the mentioned oxidizing agents can remove SO₂ to under detection limit. Results from Figure 3.2 indicate that NaClO₂ and ClO₂ are stronger oxidizers than TBHP and NaClO in oxidizing NO_x. Other major drawbacks of the TBHP scrubbing system are its thermal degradation at higher temperature and alkaline dependence, i.e., TBHP is only effective on NO_x oxidation in alkaline condition. The alkaline TBHP solutions are corrosive and can absorb the large amount of CO₂ (typically 15%) present in the FCC regenerator flue gas. To keep a high pH for the effectiveness of the scrubbing solution, alkali must be continuously added to it, resulting in a relative high cost of reagents.

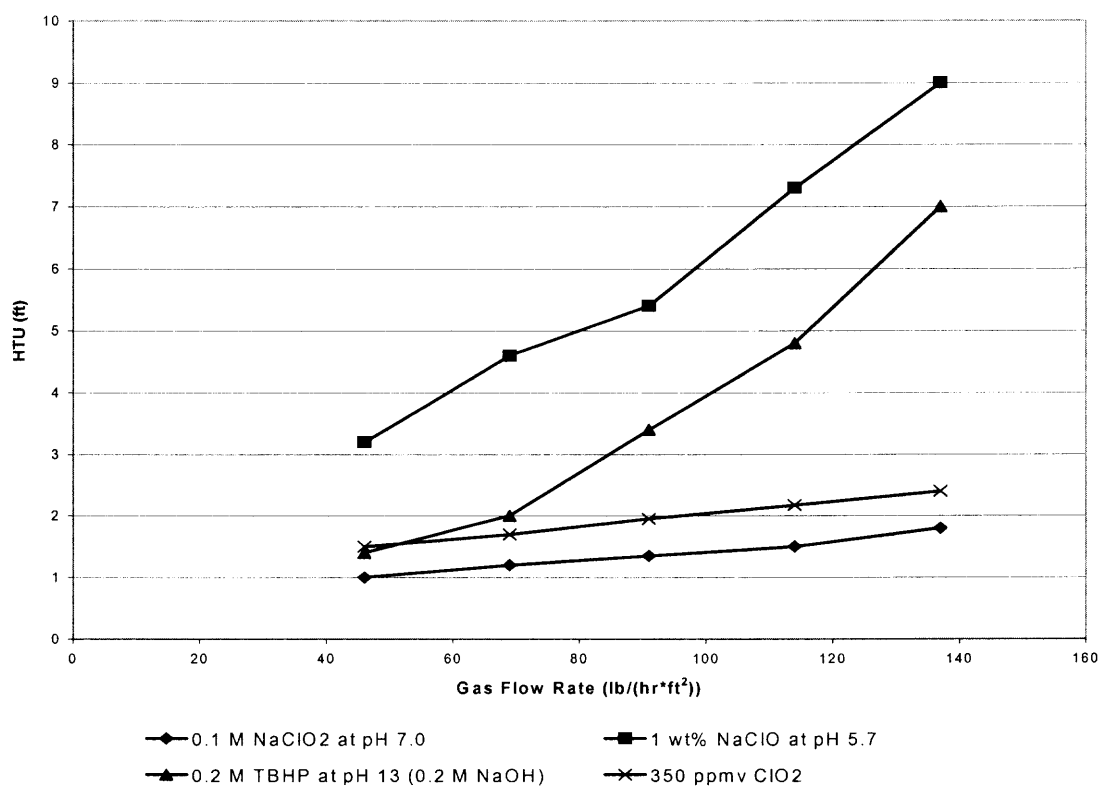


Figure 3.2 HTU Comparison Between Oxidizing Agents in Bench-scale Packed Scrubber (LFR = 2.4 LPM, Temperature = 60°C).

From Figure 3.2, ClO_2 is the strongest oxidizer among all the oxidizing agents tested. It has similar removal efficiency as that of NaClO_2 with a much lower concentration. Unfortunately, the process was found to be not feasible, due to the stripping problem of ClO_2 at higher temperatures and its complicated and expensive generation procedures. ClO_2 is very soluble in water, though it is also extremely volatile and can be easily removed from dilute aqueous solutions by a minimum of aeration^[31] or temperature increase. It was observed that 80% of ClO_2 was lost from its aqueous solution at 60°C during 9 minutes of experimental running time. Therefore, NaClO_2 was singled out for further test.

CHAPTER 4

BENCH-SCALE NO_x SCRUBBING WITH SODIUM CHLORITE SOLUTIONS

There have been a number of studies on NO_x oxidation and absorption with NaClO₂ solutions in bench-scale bubble column and packed bed reactors, which were introduced in the Chapter 2 of the dissertation. The results of these studies suggest that NaClO₂ solutions provide effective media for the oxidation and absorption of NO_x.

However, no such study has ever been done on the NO_x control from FCC regenerator effluent gases to our best knowledge. We extend these studies to the area of emission control from FCC regenerator. Our ultimate goal is to design a scrubbing system in a way that it can remove all the pollutants from the FCC regenerator, that is, NO_x, SO_x, and particulate, in the same system in a cost-efficient way.

This study was carried out in two phases in our laboratory. During the first phase, the NO_x scrubbing with NaClO₂ solutions was tested in the bench-scale packed bed and ejector Venturi systems, which provided a foundation for the subsequent study. The second phase involved NO_x scrubbing in a pilot scale scrubbing system. The reproducibility of experimental results from each system described in the dissertation was investigated though repeating a set of tests four to five times in each system. Relative Standard Deviations (%RSDs) were calculated using equation 4.1, and used to measure the reproducibility. Less than 5% of %RSDs were achieved in bench-scale systems, while up to 10% of %RSDs for pilot-scale systems.

$$\%RSD = 100 \times \sqrt{\frac{\sum (x_i - x_a)^2}{n - 1}} / x_a \quad 4.1$$

Where x_a is the average value of each measurement of x_i .

4.1 NOx Scrubbing with NaClO₂ Solutions in the Packed Bed Scrubber

Scrubbing with NaClO₂ solutions was tested on bench-scale 3'' packed scrubber with 1/2'' plastic raschig rings. The experimental set-up is the same as that described in section 3.1. SO₂, O₂, and CO₂ concentrations were similar to that expected at FCC regenerator emissions, 500 ppmv, 3%, and 15% respectively ^[32]. NOx concentrations were varied from 50 to 300 ppmv to provide a range for the real situations, depending on FCC unit operation and whether or not Thermal DeNOx is used upstream ^[32]. The scrubbing liquid was a buffered solution of NaClO₂.

For each experiment performed, the HTU and the volumetric mass transfer coefficient, K_{ga}, were calculated. HTU and K_{ga} were used to determine the effect of a number of parameters, pH, NaClO₂ concentration, temperature, and NOx inlet concentration, on the NOx oxidation and absorption. K_{ga} can be calculated from equation (4.2),

$$K_g a = \frac{F / \Omega}{HTU} \quad (4.2)$$

Results are shown in Figure 4.1 – 4.4. From these figures, the following conclusions can be made:

- Up to 90% of NOx can be removed by this system with a simultaneous 100% removal of SO₂.
- The higher the concentration of NaClO₂, the better is the control of NOx. 0.03 M is a critical point, above this concentration, HTU increases linearly with the increase of gas rate (Figure 4.1).

- NO breakthrough was only observed at the pH value of 9. HTU for NO_x removal increased with increasing solution pH. These indicate that OH⁻ inhibits the NO_x oxidation and absorption (Figure 4.2).
- The reaction between NO_x and NaClO₂ is favored at elevated temperature (Figure 4.3).
- NO_x removal efficiencies at lower NO_x inlet concentration, 60 ppm, are similar to those at higher concentration, 300 ppm. Up to 90% of NO_x removal rate with a simultaneous SO₂ removal was achieved at 60 ppm NO_x inlet concentration, which is very difficult to achieve with other NO_x treatment technologies (Figure 4.4).

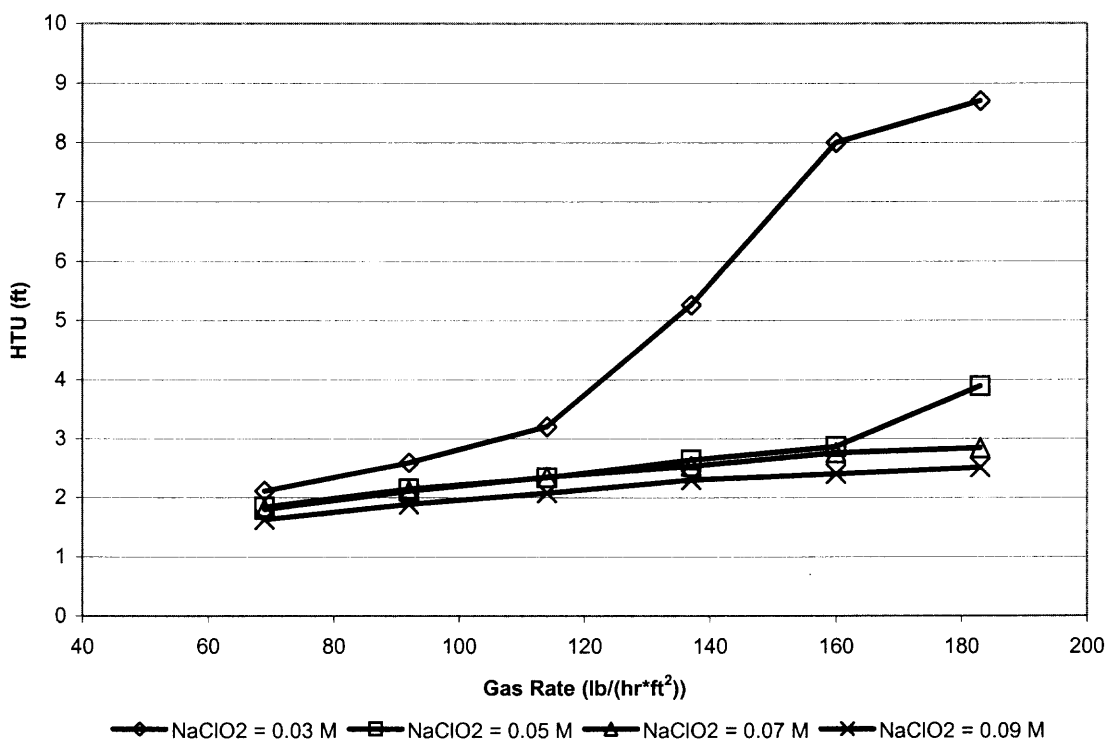


Figure 4.1 NaClO₂ Concentration Effect on NO_x Removal in Bench-scale Packed Scrubber (NO_x = 300 ppm, LFR = 2.4 LPM, pH = 7, temp = 60°C).

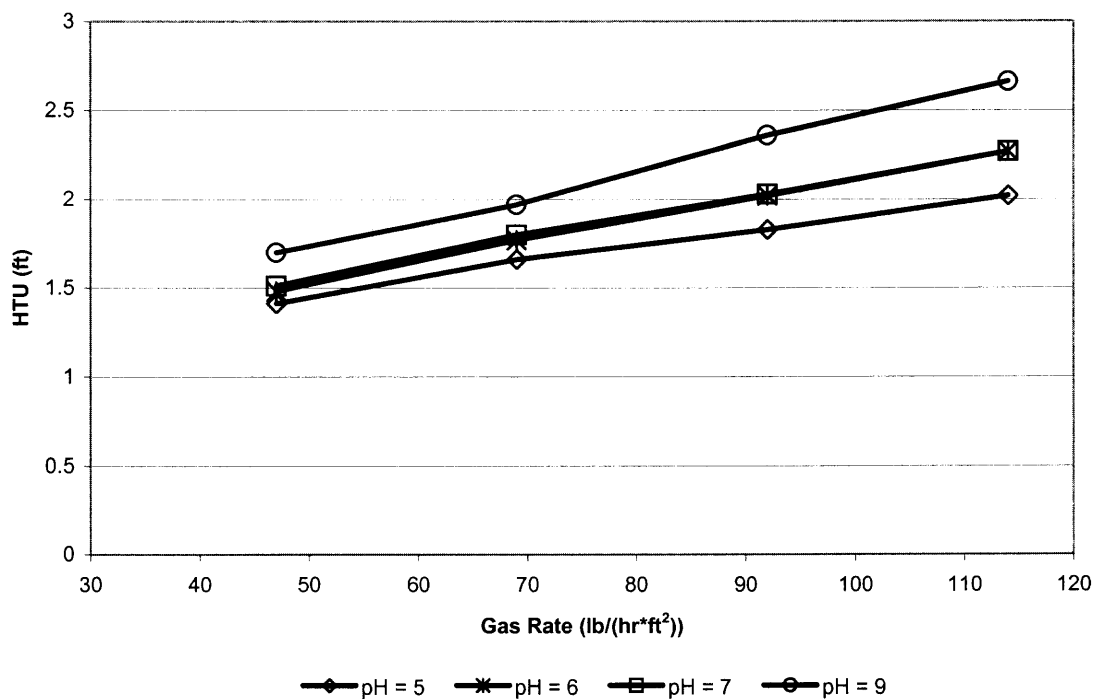


Figure 4.2 pH Effect on NO_x Removal in Bench-scale Packed Bed Scrubber (NaClO₂ = 0.1 M, NO_x = 300 ppm, LFR = 2.4 LPM, Temp = 20°C).

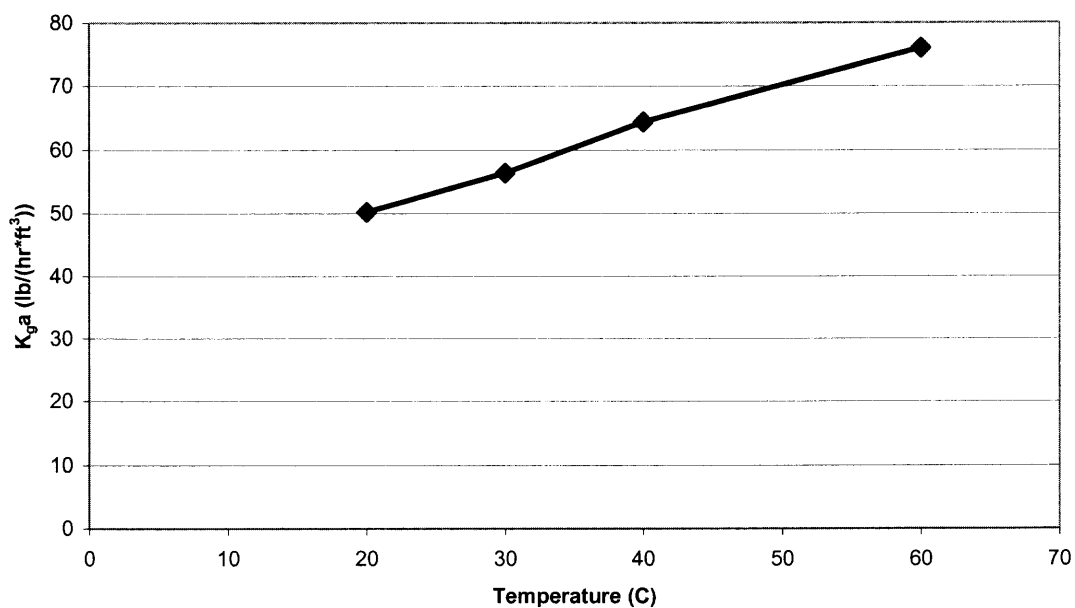


Figure 4.3 Temperature Effect on NO_x Removal in Bench-scale Packed Scrubber (NaClO₂ = 0.1 M, pH = 7, Gas Rate = 114 lb/(hr*ft²), LFR = 2.4 LPM).

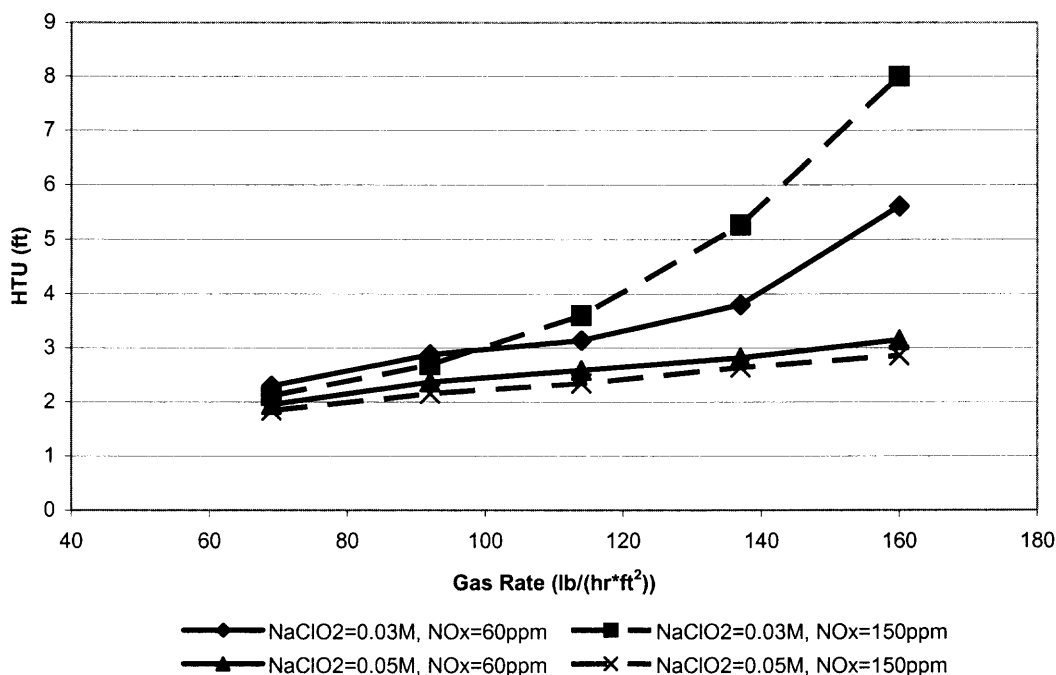


Figure 4.4 NO_x Inlet Concentration Effect on NO_x Removal in Bench-scale Packed Scrubber (LFR = 2.4 LPM, pH = 7, Temp = 60°C).

4.2 NO_x Scrubbing with NaClO₂ Solutions in an Ejector Venturi Scrubber

We extended our studies by conducting scrubbing experiments in a bench-scale ejector Venturi scrubber, to remove both particulate and gaseous pollutants from FCC regenerator in the same system.

4.2.1 Ejector Venturi Scrubber

The ejector Venturi scrubber utilizes a high velocity liquid spray to pump the gas, remove particulate and absorb objectionable gases ^[33]. It provides a higher interfacial area (due to finer droplet size) compared to the conventional high-energy Venturi scrubber ^[33], and thereby increasing the rate of mass transfer as a desirable attribute for functioning as a gas absorber at the same time of particulate collection. Its advantages also include: 1)

relatively simple design and low capital cost; 2) ability to handle large flow rates of gas in relatively small equipment; 3) ability to handle slurry absorbents ^[34]. Consequently, ejector Venturi scrubbers find applications wherever simultaneous control of particulate and gaseous pollutants is needed as in the case of a FCC regenerator. However, only a few theoretical and experimental studies of gas absorption in Venturi scrubbers were found in the literature, and most of these studies were for high-energy Venturi scrubbers and for SO₂ absorption ^[33 – 40]. In one paper found for ejector Venturi scrubber, the volumetric mass transfer coefficient (K_{ga}) and the interfacial area were calculated for the SO₂ – NaOH absorption system ^[33]. Adewuyi ^[36] did some work on SO₂ effect on NO_x oxidation and absorption in ejector Venturi scrubber. He found that SO₂ enhanced NO absorption for non-buffered NaClO₂ solution. In our Venturi scrubbing system, aqueous NaClO₂ solutions were used for the removal of NO_x and SO₂ from gas streams with composition similar to that of flue gas from a FCC regenerator. Experimental results showed that up to 90% of the NO_x could be removed by this system, with a simultaneous 100% removal of SO₂. Experiments were also conducted using a feed with composition similar to that of effluent from a Thermal DeNO_x pretreatment. The low concentration of NO_x after pretreatment can be removed in the system, and solutions with very low concentrations of nitrate and chloride were generated, which is especially environmentally sound.

4.2.2 Experimental Section

The experimental set-up is similar to that described in section 3.1, except that an ejector Venturi scrubber was used as the gas scrubber instead of the packed bed. Figure 4.5 shows the schematic diagram of the experimental system.

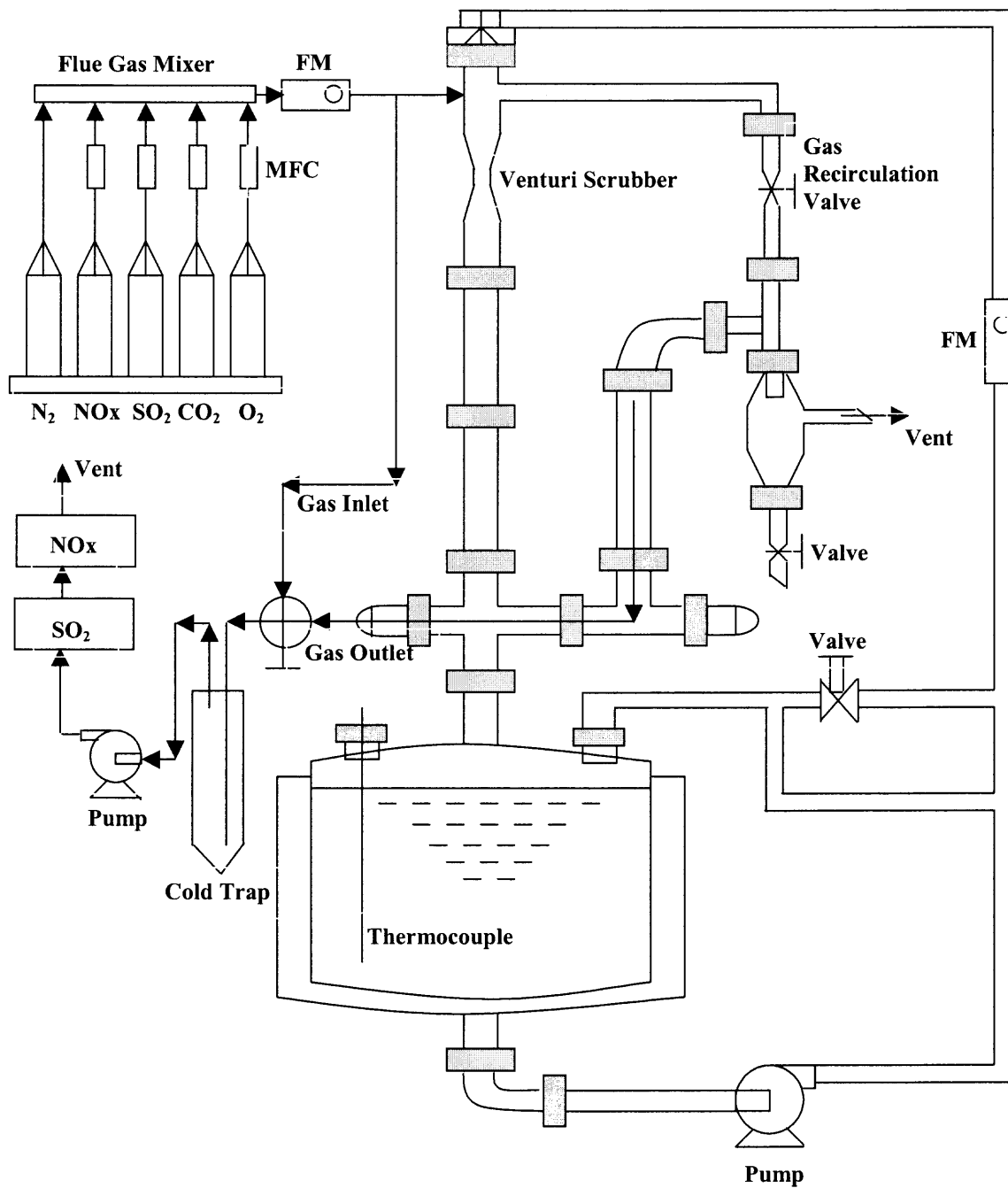


Figure 4.5 The Schematic Diagram of the Ejector Venturi Scrubbing System.

The ejector Venturi Scrubber consists of convergent, throat, and divergent sections. The diameter of the Venturi is 2 inch with an overall height of 26.5 inch. The throat diameter is 20 mm, and the length of the throat is 1 inch. Scrubber liquor is supplied by a rotary lobe pump with a capacity of 1-20 gal per minute (GPM). As a result of the large liquid pressure across the nozzle (a TG series Unijet full cone spray), a high velocity liquid spray exits the nozzle. In addition, the velocity of the liquid spray creates a low pressure region or vacuum, which pulls the gas into the scrubber.

In this system, a U-tube and a 20-liter empty space above the scrubbing solution surface in a solution tank are used as a separator. The scrubbing liquid is drained to the tank and recycled back to the spray nozzle by the water pump. The solution in the tank can be heated up to 100°C by a heating mantle connected to a Model PL724 automatic temperature controller. The flue gas can also be recirculated through the Venturi system through a loop design. The gas recirculation is controlled by a valve installed along the loop.

One hundred liters of scrubbing solution was used to run these experiments in a semi-batch mode with continuous flue gas injection. The liquid flow rate was controlled by a reflux valve and measured by a Rota meter installed on the water recycle line. The exiting gas was carried to the analyzers after moisture condensation at 0°C. A sampling port on the solution tank was used to collect liquid samples for analysis.

4.2.3 Results and Discussion

The results of the Ejector Venturi scrubbing experiments are given in this section. Operating parameters, such as gas flow rate, liquid flow rate, pH, operating temperature, gas phase compositions (NO, NO₂, SO₂, CO₂ and O₂), concentration of sodium chlorite,

and gas recirculation, were studied for their effects on NOx oxidation and absorption in the ejector Venturi scrubber. The gas removal efficiency, E, is calculated from equation (4.3):

$$E = 1 - \frac{y_{out}}{y_{in}} \quad (4.3)$$

Where y_{in} is the inlet solute gas mole fraction, and y_{out} is the outlet solute gas mole fraction.

Chemical reaction in the liquid phase reduces the equilibrium partial pressure of the solute over the solution, which greatly increases the driving force for mass transfer. If the reaction is essentially irreversible at absorption conditions, as in the case of oxidation of NOx by NaClO₂, the equilibrium partial pressure is zero, and the overall NOx absorption rate, N, is as follows:

$$N = K_g a Y_{lm} \quad (4.4)$$

Where $K_g a$ is the volumetric mass transfer coefficient based on the overall gas-phase driving force. Y_{lm} is the log mean concentration driving force and is determined from the inlet and outlet solute gas mole fractions, Y_{in} and Y_{out} using equation 4.5 ^[35]:

$$Y_{lm} = \frac{Y_{in} - Y_{out}}{\ln(Y_{in} / Y_{out})} \quad (4.5)$$

N can be calculated from experimental results using equation (4.6),

$$N = Q_g (Y_{in} - Y_{out}) / V \quad (4.6)$$

Where Q_g is the mass flow rate of gas phase, and V is the volume of the Venturi scrubber, which is 0.9 liter.

From equation (4.3) - (4.5), $K_g a$ can be calculated from equation (4.7),

$$K_g a = \frac{Q_g \ln(Y_{in} / Y_{out})}{V} \quad (4.7)$$

In this part, the volumetric mass transfer coefficients for NO_x oxidation and absorption in the Venturi system were correlated to gas rate for evaluating the efficiency of the scrubbing system under variable operating conditions and for further scale-up design.

4.2.3.1 Effects of Liquid Flow Rate and Gas Flow Rate. In ejector Venturi scrubber, the high velocity of liquid pumped through the system may play a more important role on absorption than it does in other scrubbing systems. Atay^[33] observed a sharp increase in efficiency as the liquid flow rate reaches the complete atomization.

In our study, experiments were conducted in the Venturi system with a NaClO₂ concentration of 0.01 M at pH of 6.0 at room temperature. Simulated flue gases with a composition of 250-300 ppmv of NO_x, 450 – 500 ppmv of SO₂, and 3% in volume of O₂ in nitrogen balance gas, were injected in the system. Four gas flow rates, 15, 22, 29, and 36 liter/min, and five liquid flow rates, 1, 2, 3, 4, and 5 gallon/min, were run in the experiments. No SO₂ breakthrough was observed in the experiments, and no N₂O was detected by the FTIR.

Figure 4.6 shows the variation with liquid flow rate of the scrubbing efficiency of the ejector Venturi scrubber. There is obvious improvement of NO_x removal efficiency with the increase in LFR. However, no sharp increase in removal rate was observed as LFR increased, possibly because of a limitation of our apparatus which presented difficulties in running liquid flow rates lower than 1 GPM.

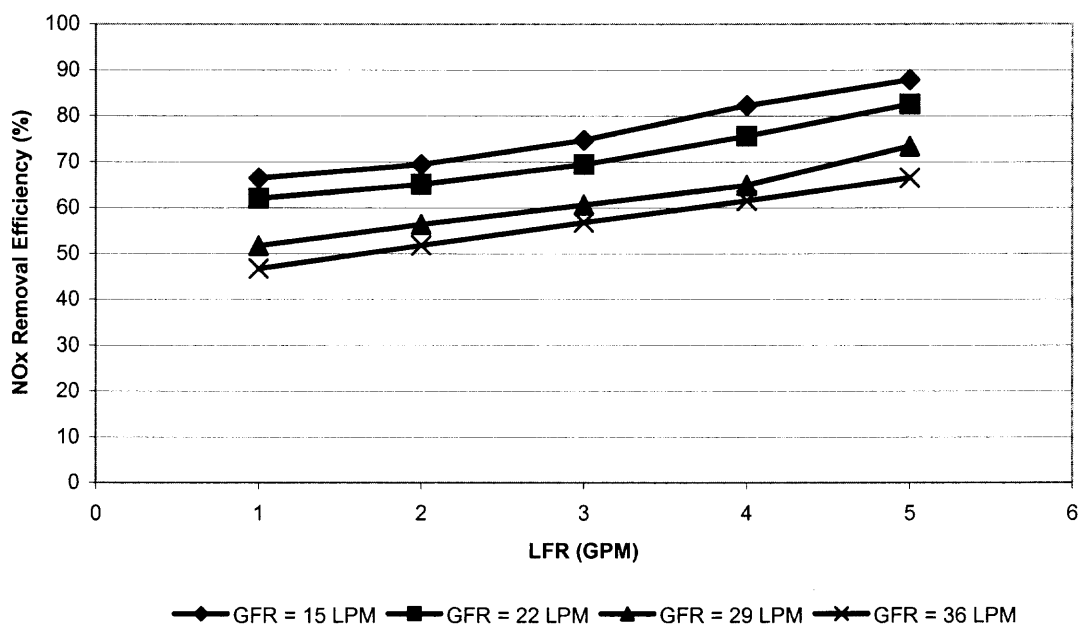


Figure 4.6 Liquid Flow Rate Effect on NOx Removal in Venturi Scrubber ($\text{NaClO}_2 = 0.01 \text{ M}$, $\text{pH} = 6$).

The variation of the volumetric mass transfer coefficient, K_{ga} , with gas flow rate is shown in Figure 4.7.

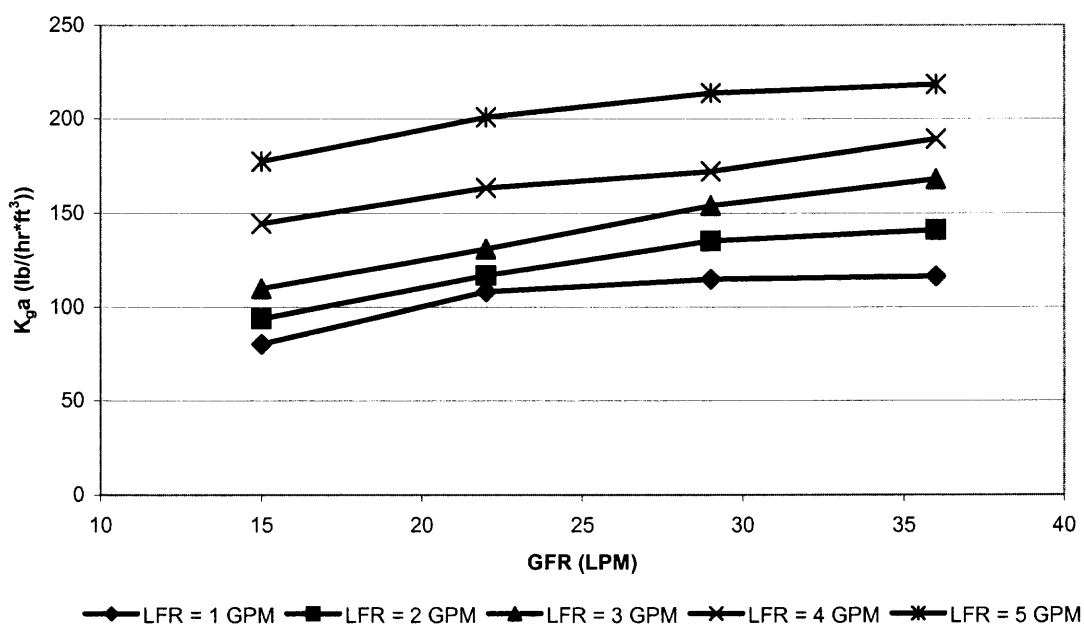


Figure 4.7 K_{ga} vs. GFR in Venturi Scrubber ($\text{NaClO}_2 = 0.04 \text{ M}$, $\text{pH} = 7$).

The implication of the observation that the K_{ga} increased with the gas flow rates is evidence of the validity of our assumption of instantaneous and irreversible chemical reaction between NO_x and NaClO_2 at absorption conditions. Higher gas flow rates within our test range improve the mixing of gas and liquid in the system, and the low residence time has less effect on the NO_x absorption due to the very fast chemical reaction, compared with the improvement caused by better mixing up.

4.2.3.2 pH effect. pH plays an important role in the oxidation and absorption of NO_x by NaClO_2 from others studies. Based on a study by Yang ^[11], it is believed that a high concentration of NaOH will inhibit the NO oxidation and absorption. For the application of NO_x removal in FCC regenerators, pH control is critical for not absorbing CO_2 , which represents 15% of the flue gas ^[32], in a consideration of cost saving. Therefore, experiments were run to determine the pH effects on the NO_x oxidation and absorption by NaClO_2 .

Experiments were conducted in the Venturi system with NaClO_2 concentration of 0.01 M at room temperature. Simulated flue gases with a composition of 250-300 ppmv of NO_x , 450 – 500 ppmv of SO_2 , and 3% in volume of O_2 in nitrogen balance gas, were injected in the system. Four gas flow rates, 15, 22, 29, and 36 liter/min, with a liquid flow rate of 4 gallon/min, were run in each experiment. Five pH values, 5.0, 6.0, 7.0, 8.0, and 9.0, were tested, and the variation of K_{ga} with GFR is shown in Figure 4.8. No SO_2 breakthrough was observed, and no N_2O was detected by the FTIR. Breakthrough of NO was observed at higher range of pH value from 7.0 to 9.0, which indicates that OH^- inhibit the NO oxidation and absorption. It is also obvious from the figure that as pH increases, the rate at which K_{ga} increases level off, and at pH of 9.0, the K_{ga} even

decreases with the increase of gas flow rate. That further confirmed the inhibition effect of OH^- on NO_x oxidation and absorption. The reaction between NO_x and NaClO_2 can not be considered as an instantaneous and irreversible reaction at higher pH, thus longer residence time, which means longer reaction time, can achieve better absorption.

Figure 4.8 indicates that this scrubbing system is more efficient under a slightly acidic condition, which can be taken as an advantage of the wet scrubbing treatment of the FCC regenerator effluent over other technologies. This media can remove NO_x and SO_2 simultaneously without absorbing CO_2 into the scrubbing solutions.

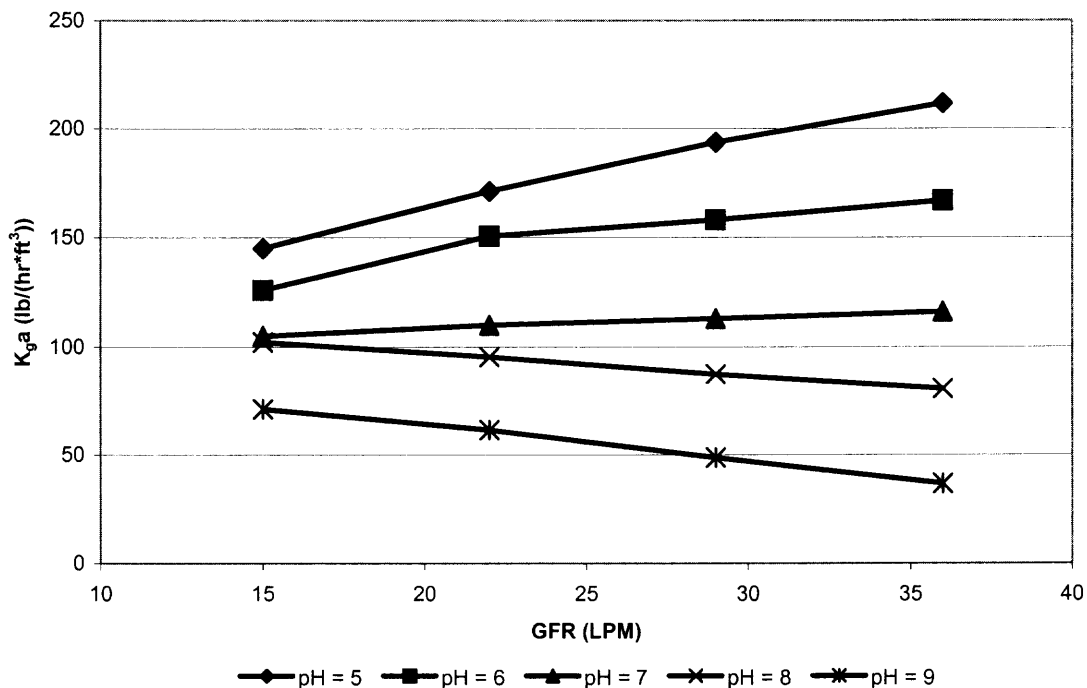


Figure 4.8 pH Effect on NO_x Removal in Venturi Scrubber ($\text{NaClO}_2 = 0.01 \text{ M}$, $\text{LFR} = 4 \text{ GPM}$).

4.2.3.3 NaClO_2 Concentration Effect. The effect of NaClO_2 concentration on NO_x oxidation and absorption was studied in order to better understand operating costs for process design consideration. Experiments were conducted with four different NaClO_2

concentrations, 0.01, 0.02, 0.04, and 0.06 M, at pH of 7.0 at room temperature. Simulated flue gases with a composition of 250-300 ppmv of NO_x, 450 – 500 ppmv of SO₂, and 3% in volume of O₂ in nitrogen balance gas, were injected in the system. Four gas flow rates, 15, 22, 29, and 36 liter/min, with a liquid flow rate of 4 gallon/min, were run in each experiment. No SO₂ breakthrough was observed in the experiments, and no N₂O was detected by the FTIR.

The NaClO₂ concentration effect on NO_x removal is shown in Figure 4.9. Higher concentration of NaClO₂ gives better removal efficiency of NO_x, which is consistent with other studies in this field. However, in addition to the lower utilization rate, high concentration scrubbing solutions also end up with high concentrations of NO₃⁻ and Cl⁻ in spent solutions, which may lead to corrosion or pollution problems and may need further treatment before discharge. Therefore, an optimal concentration of NaClO₂ must be selected carefully with the balance of removal efficiency and operating cost.

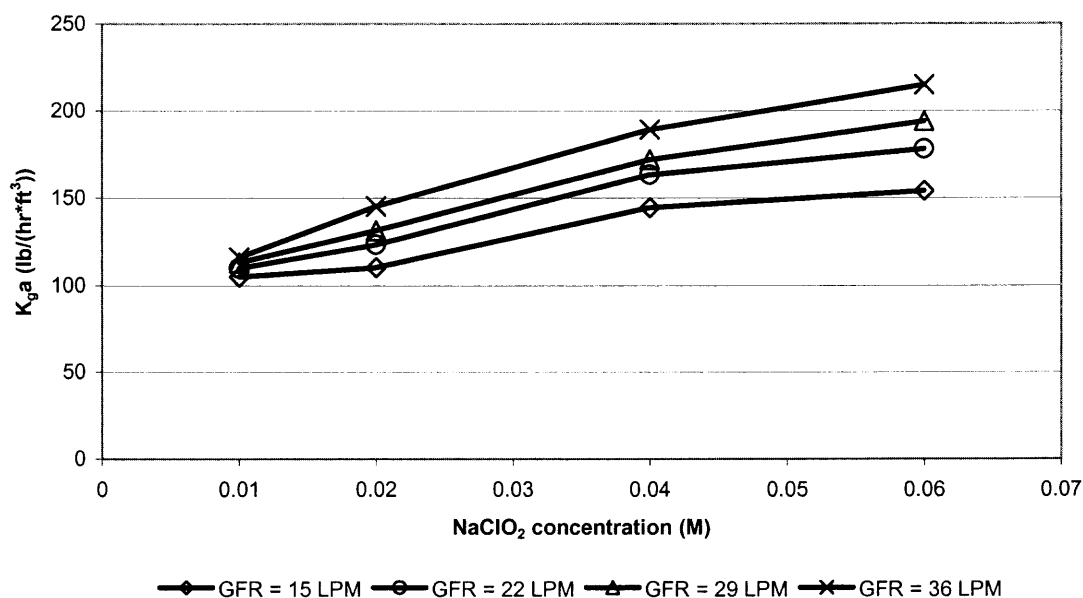


Figure 4.9 NaClO₂ concentration Effect on NO_x Removal in Venturi Scrubber (pH = 7, LFR = 4 GPM).

4.2.3.4 Temperature Effect. FCC regenerator flue gas generally enters a scrubber at a temperature of 430 - 530°F ^[32]. Chemical reactions, especially oxidation, are enhanced by high temperature but not gas absorption. Normally, the solubility of a gas decreases with the increasing temperature. Therefore, temperature effect on NO_x oxidation and absorption is one of the uncertainties in the design of a scrubber. Experiments were conducted at three different temperatures, 20°C, 40°C, and 60°C, with a NaClO₂ concentration of 0.01 M at pH of 7.0. Simulated flue gases with a composition of 250-300 ppmv of NO_x, 450 – 500 ppmv of SO₂, and 3% in volume of O₂ in nitrogen balance gas, were injected in the system. Four gas flow rates, 15, 22, 29, and 36 liter/min, with a liquid flow rate of 3 gallon/min, were run in each experiment. No SO₂ breakthrough was observed in the experiments, and no N₂O was detected by the FTIR. The temperature effect on NO_x removal is shown in Figure 4.10.

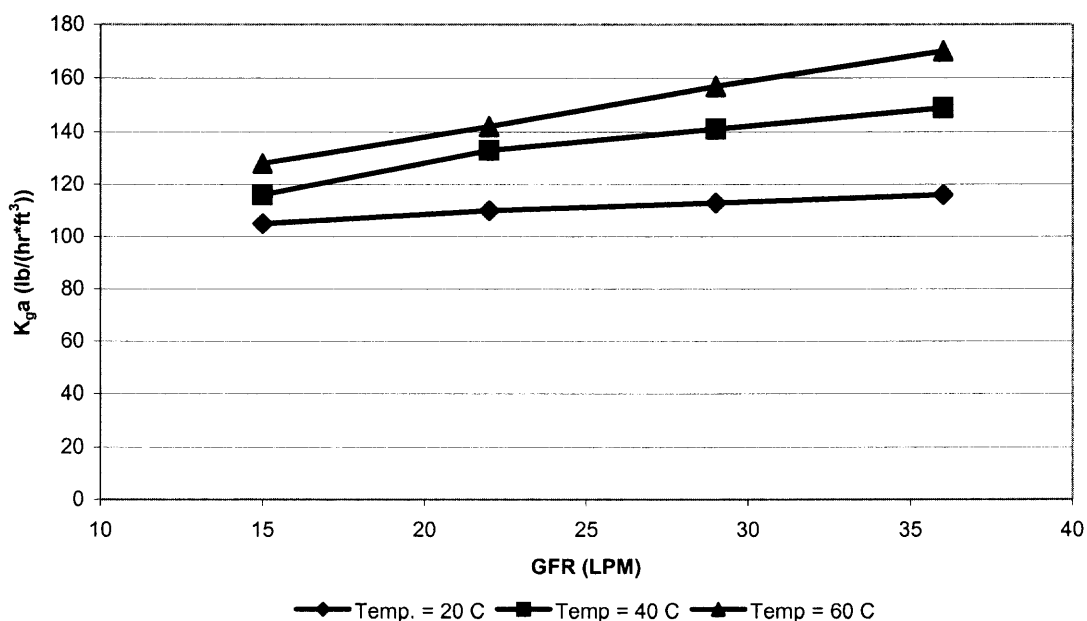


Figure 4.10 Temperature Effect on NO_x Removal in Venturi Scrubber (NaClO₂ = 0.01 M, pH = 7, LFR = 4 GPM).

The results show that as temperature increases K_{ga} increases as a result of enhanced oxidation reactions of NO_x with NaClO_2 . Thus, the heat energy of the effluent gas from FCC regenerator is anticipated as a positive that can be used to achieve better removal efficiency.

4.2.3.5 NO_x Inlet Concentration Effect. As mentioned before, this scrubbing process is especially environmentally sound when it is used after a Thermal De NO_x pretreatment. Therefore, a few experiments were conducted to treat flue gases with lower NO_x inlet concentrations, 50 – 80 ppmv, which are typical in the effluent from Thermal De NO_x [32]. Experiments were conducted in the Venturi system with NaClO_2 concentrations of 0.01 and 0.04 M at pH of 7.0 at room temperature. Simulated flue gases with a composition of 50-80 ppmv of NO_x , 450 – 500 ppmv of SO_2 , and 3% in volume of O_2 in nitrogen balance gas, were injected in the system. Four gas flow rates, 15, 22, 29, and 36 liter/min, with a liquid flow rate of 4 gallon/min, were run in each experiment. No SO_2 breakthrough was observed in the experiments, and no N_2O was detected by the FTIR. The comparison of the efficiencies with the lower and higher range of NO_x inlet concentration at different NaClO_2 concentrations is shown in Figure 4.11.

From these results, at low concentration of NaClO_2 , the higher the NO_x inlet concentration, the lower the removal efficiency due to the insufficient oxidant in the solution. With the increase in oxidant concentration, the difference decreases, and at concentration of 0.04M, almost the same efficiencies were achieved for the lower and higher range of NO_x inlet concentrations. Up to 85% of NO_x removal efficiency at as low as 50 – 80 ppm of NO_x inlet concentration with a simultaneous removal of SO_2 can be easily achieved in the scrubbing system, which is very difficult for other NO_x

treatment technologies. Furthermore, a slightly acidic solution can also absorb NH_3 , which may escape from the DeNOx system.

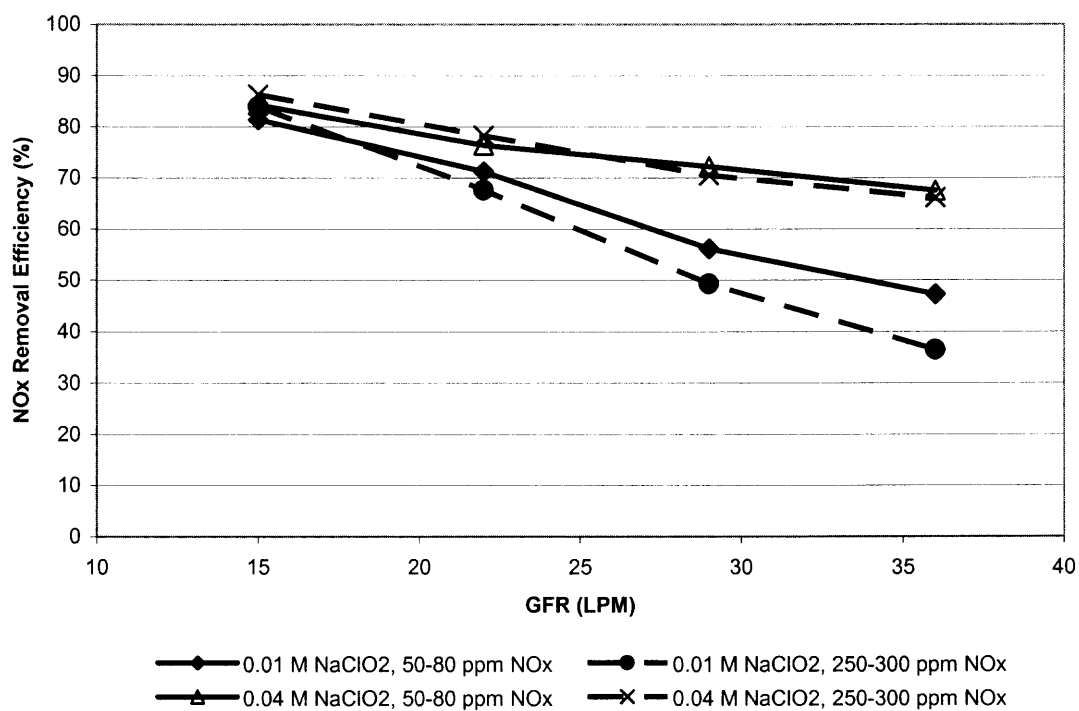


Figure 4.11 NO_x Inlet Concentration Effect on NO_x Removal in Venturi Scrubber (pH = 7, LFR = 4 GPM).

4.2.3.6 Effect of Gas Recirculation. With the gas recirculation valve open, the flue gas can be recycled within the system before finally venting to the outside. This simple design is anticipated to improve the gas reaction and absorption due to the longer contact time. Also anticipated is a decrease in the system pressure build up, allowing the system to operate at much higher gas flow rates. Figure 4.12 shows the gas recirculation effect on NO_x oxidation and absorption. The experiments were conducted in the Venturi system with a NaClO₂ concentration of 0.04 M at pH of 7.0 at room temperature with the gas recirculation valve open. Simulated flue gases with a composition of 250-300 ppmv of NO_x, 450 – 500 ppmv of SO₂, and 3% in volume of O₂ in nitrogen balance gas, were

injected in the system. Eight gas flow rates, 15, 22, 29, 36, 44, 51, 58, and 65 liter/min, with a liquid flow rate of 4 gallon/min, were run in each experiment. No SO_2 or NO breakthrough was observed in the experiments, and no N_2O was detected by the FTIR.

With gas recirculation, the NO_x removal efficiency decreases with the increase of gas flow rate much slower than it does in the case without gas recirculation, indicated by the smaller slope of the curve. This can be a considerable advantage since the operating cost will be lowered by treating larger amounts of flue gas without sacrificing much efficiency.

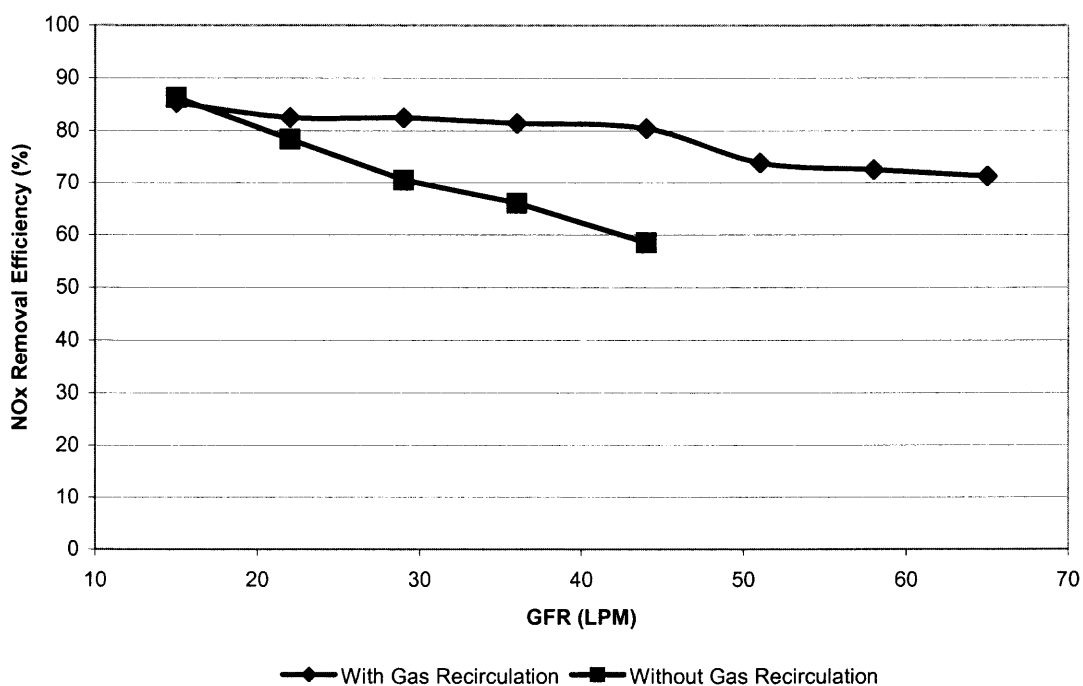


Figure 4.12 Gas Recirculation Effect on NO_x Removal in Venturi Scrubber ($\text{NaClO}_2 = 0.04 \text{ M}$, LFR = 4 GPM, pH = 7).

CHAPTER 5

PILOT-SCALE NO_x SCRUBBING WITH NaClO₂ SOLUTIONS

Based on the bench-scale study, a pilot-scale scrubbing system was set up for scale-up tests of removing NO_x with NaClO₂ solutions.

5.1 Experimental Section

The testing apparatus consists of a flue gas generation system, a scrubber, and the analytical train. The flue gas generation system is capable of simulating FCC regenerator flue gas with a capacity of 100 – 1,000 ft³/min from a blower and high-pressure gas cylinders.

The scrubber is a 2-foot diameter and 13.25 feet high fiber glass tower. The packing is 5 feet of Glitsch Grid EF-25A SS and a spray assembly consisting of 6 BETE TF 10 NN nozzles. The grid is removable for the purpose of transforming the packed bed scrubber into a mist spray scrubber. In the mist scrubber mode, a 5.75 feet spray tree was installed instead of the grid. Twelve BETE PJ40 nozzles were installed along the tree. These nozzles can generate cone-shaped fog with droplet size about 100 microns. Figure 5.1a and 5.1b represent the set-up of the pilot scale packed bed and mist scrubber respectively. A 6-inch mist eliminator and a chimney tray for collecting circulation liquid were installed both in the packed bed and mist scrubbers.

The tower was equipped with a 200 liter solution tank, a turbine pump with a capacity of 1 – 25 GPM and a head pressure out-put up to 180 psi (The high pressure pump out-put is required by the PJ40 nozzles for generating fine mist).

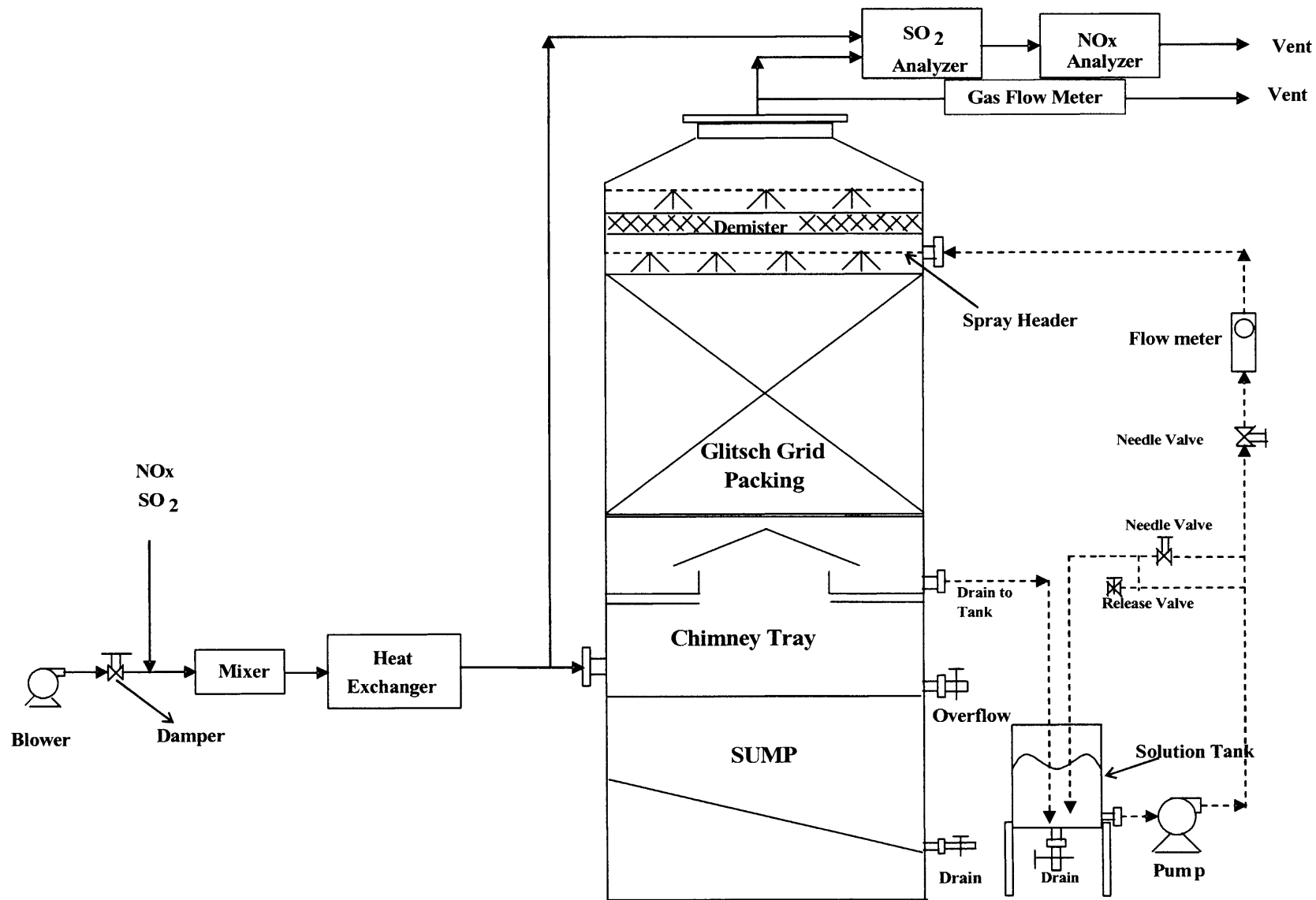
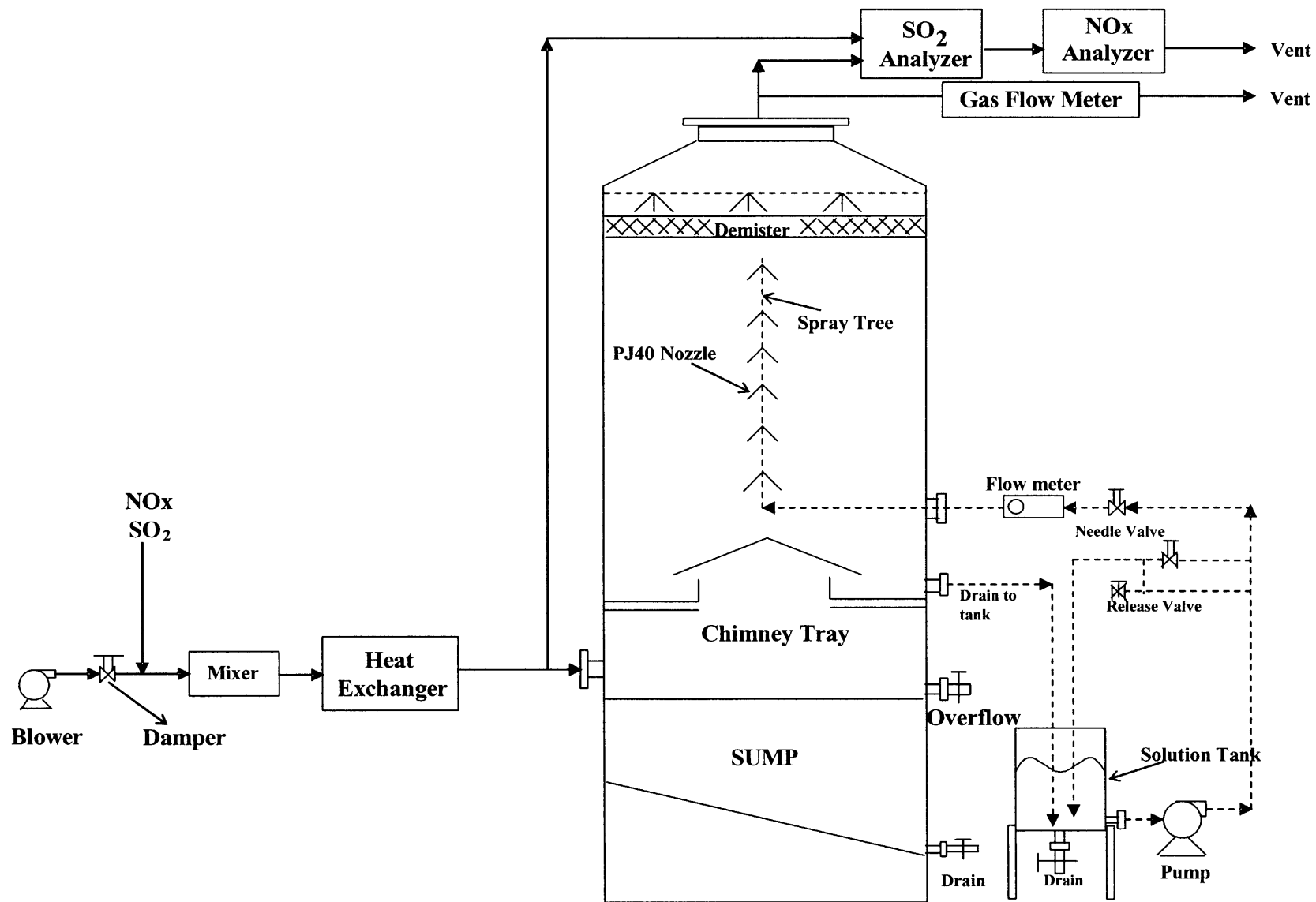


Figure 5.1a The Schematic Diagram of the Pilot-Scale Packed Scrubbing System.

Figure 5.1b The Schematic Diagram of the Pilot-Scale Mist Scrubbing System.



One hundred and fifty liters of scrubbing solution was used to run the tests in a semi-batch mode with continuous flue gas injection. The liquid flow rate is controlled by a needle valve and measured by an OMEGA FTB-905 liquid turbine flow meter with DPF701 6 – Digit Rate Meter/Totalizer. The gas flow rate is controlled by a damper immediately after the blower and measured by a gas flow meter using an orifice plate mounted on the flue gas duct.

5.2 Results and Discussions

NO and NO_x removal efficiency versus height of transfer unit were correlated to the gas rate for the pilot-scale tests.

5.2.1 Pilot-Scale Packed Bed Scrubber

The scrubber was operated at gas flow rates of 140 to 910 ft³/min with a composition of 100 – 110 ppm NO_x in air. The scrubbing solutions were buffered aqueous solutions with 0.04 – 0.3 M of NaClO₂. Up to 100% of NO removal and 85% of NO_x removal were achieved in the pilot-scale packed bed system. NO breakthrough was observed at high gas flow rates and NO₂ was always present in the outlet flue gas. Experimental results are shown in Figure 5.2 – 5.7. Increases in NaClO₂ concentration and operating temperature both enhance the oxidation and absorption rate of NO and NO_x in the system. HTU for NO oxidation is a linear function of gas rate only with NaClO₂ concentrations above 0.1 M. Solutions with NaClO₂ concentration lower than 0.1 M are not effective in treating large amount of flue gas. Liquid flow rate has little effect on NO_x removal. Lower concentration of inlet NO_x can be removed with similar efficiency as higher concentration of inlet NO_x.

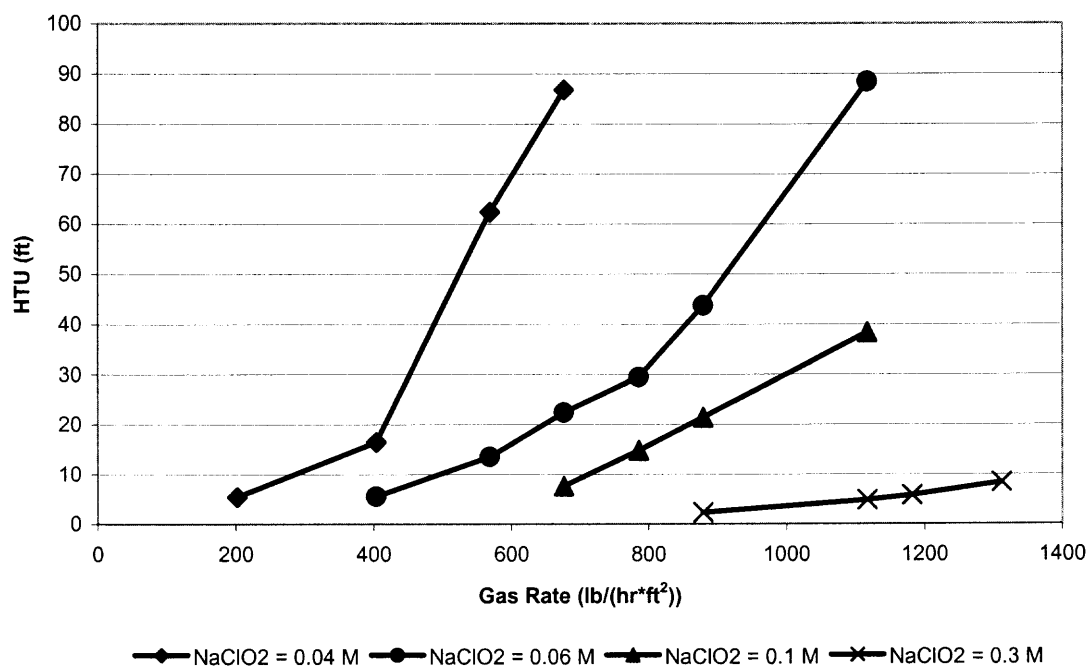


Figure 5.2 NaClO₂ Concentration Effect on NO Removal in Pilot Packed Scrubber (pH = 8, LFR = 7 GPM).

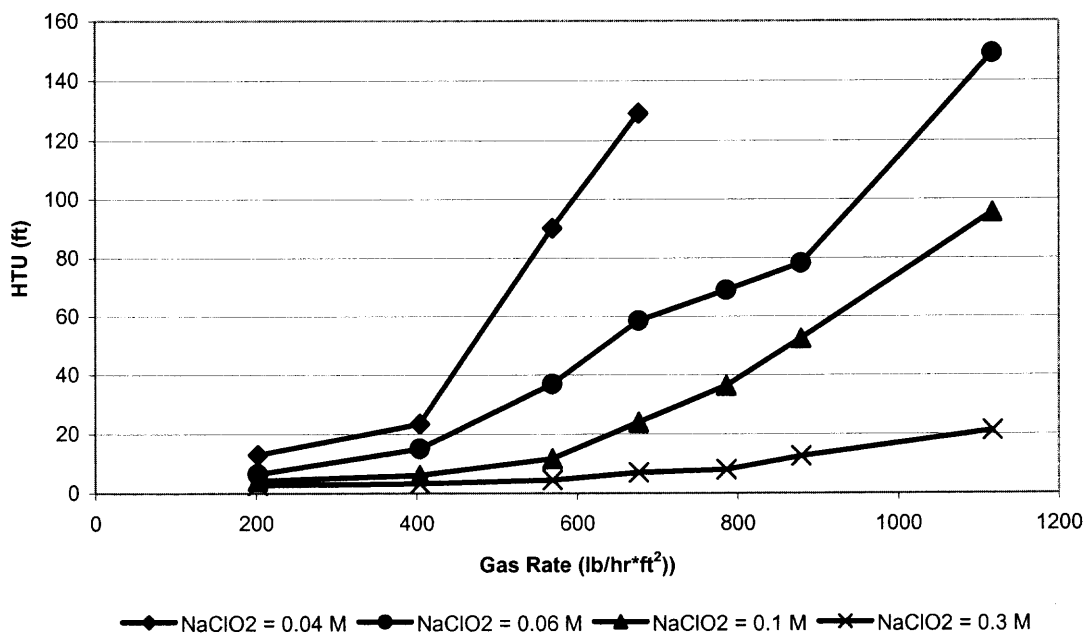


Figure 5.3 NaClO₂ Concentration Effect on NO_x Removal in Pilot Packed Scrubber (pH = 8, LFR = 7 GPM).

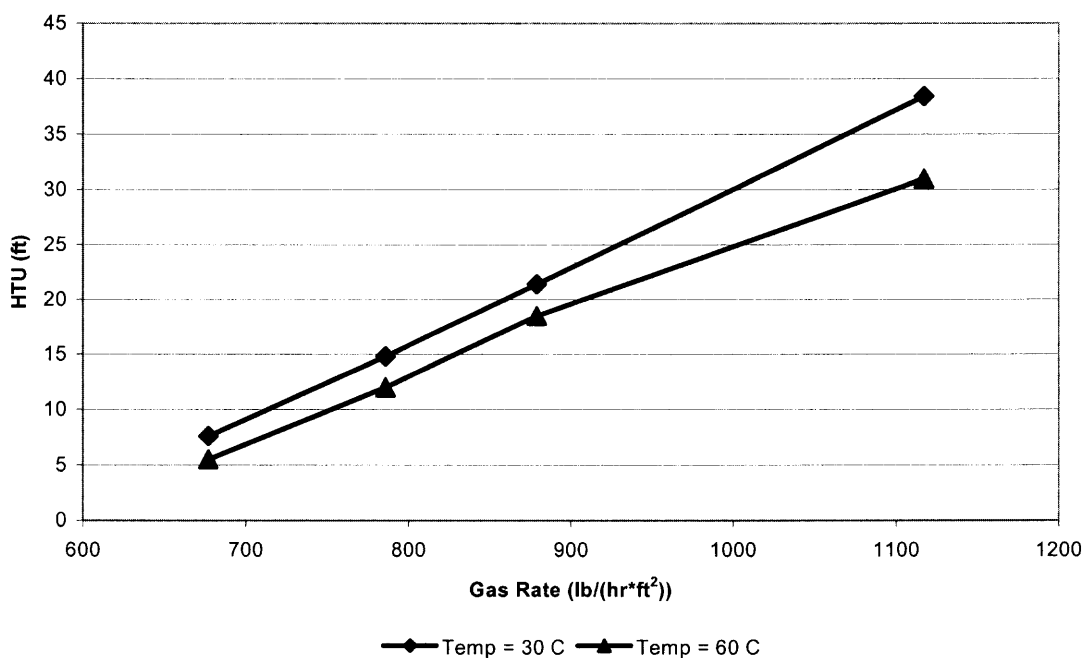


Figure 5.4 Temperature Effect on NO Removal in Pilot Packed Scrubber ($\text{NaClO}_2 = 0.1$ M, pH = 8, LFR = 7 GPM).

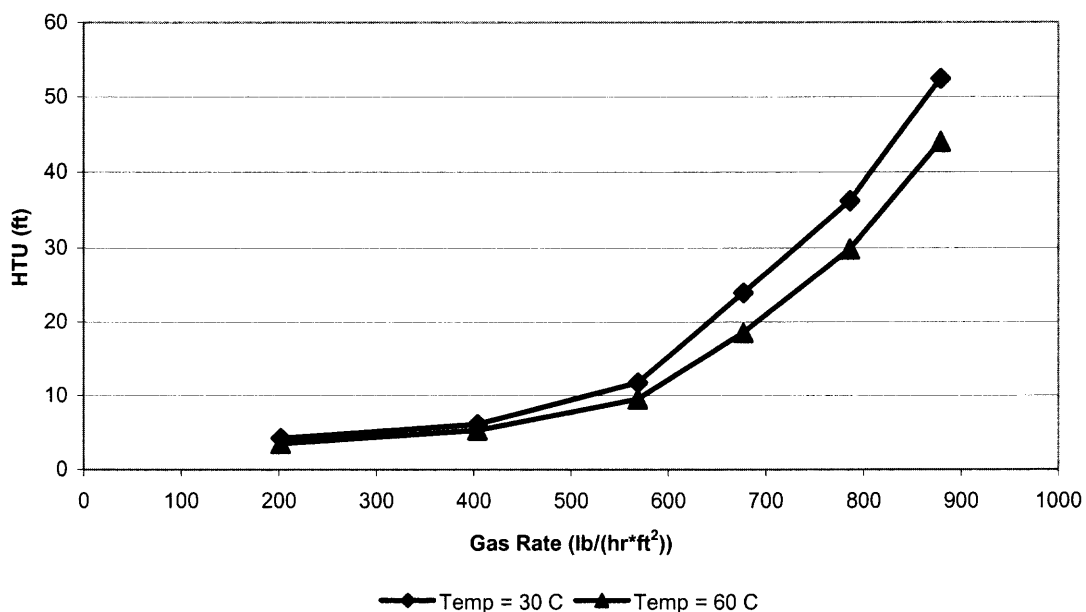


Figure 5.5 Temperature Effect on NO_x Removal in Pilot Packed Scrubber ($\text{NaClO}_2 = 0.1$ M, pH = 8, LFR = 7 GPM).

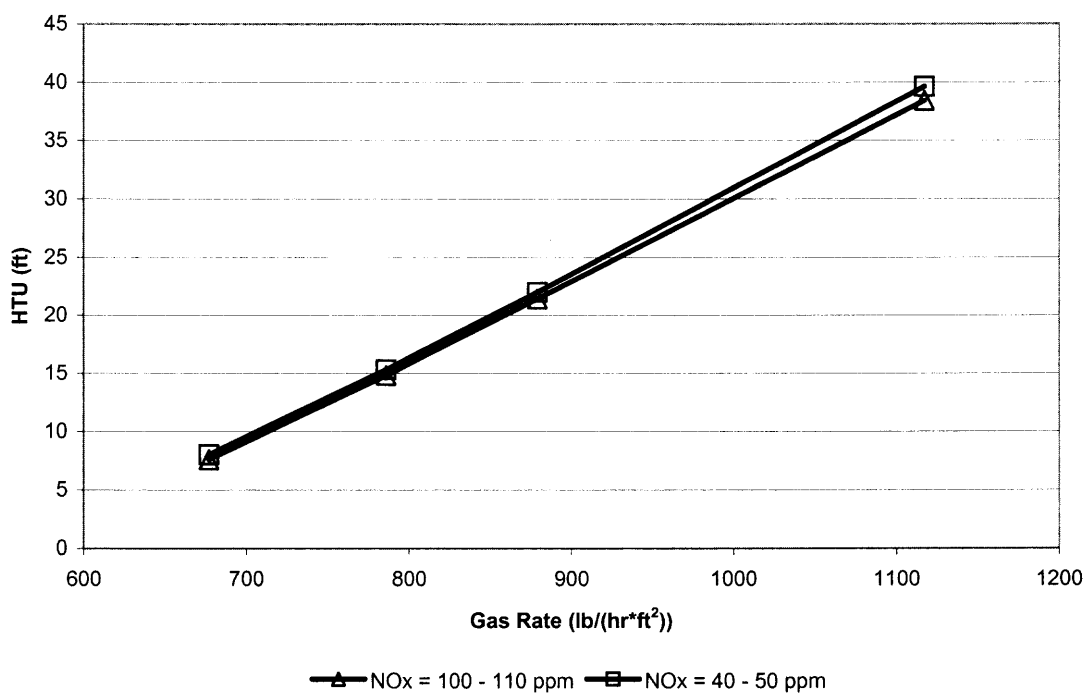


Figure 5.6 NO_x Inlet Concentration Effect on NO Removal in Pilot Packed Scrubber (NaClO₂ = 0.1 M, pH = 8, LFR = 7 GPM).

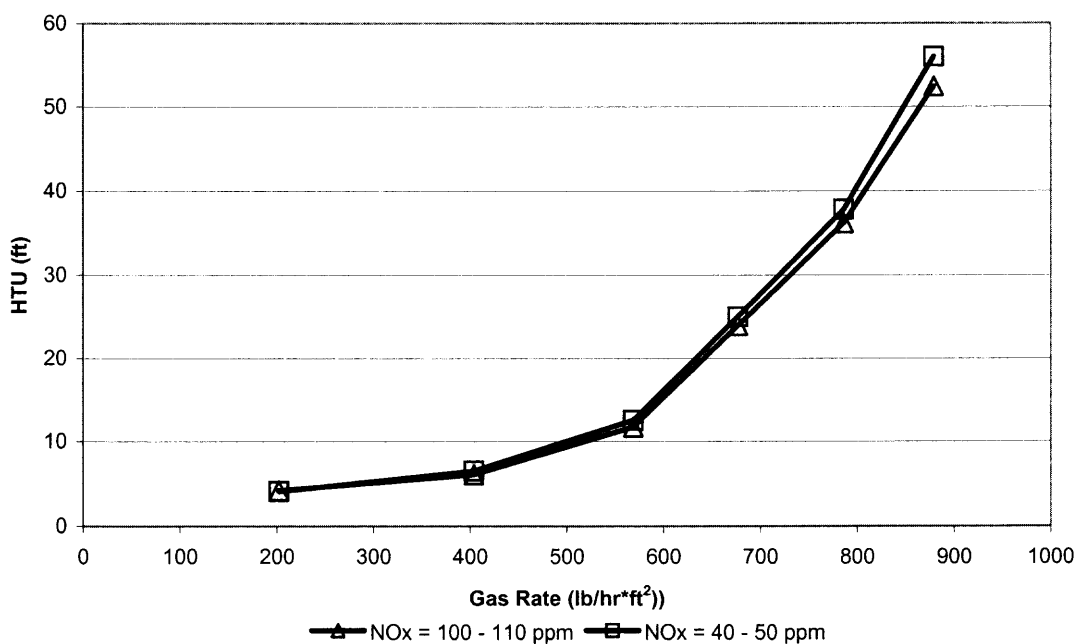


Figure 5.7 NO_x Inlet Concentration Effect on NO_x Removal in Pilot Packed Scrubber (NaClO₂ = 0.1 M, pH = 8, LFR = 7 GPM).

The typical component of FCC regenerator flue gas, SO_2 , plays a very important role in NO_x scrubbing with NaClO_2 . Figure 5.8 and 5.9 indicate that SO_2 substantially increase the reaction rate of NO_x with NaClO_2 .

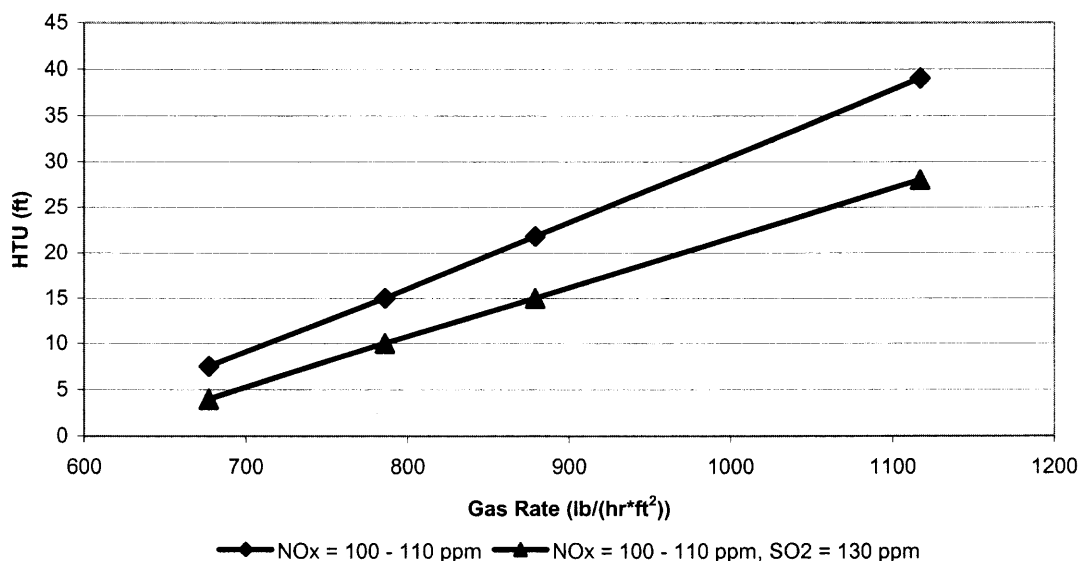


Figure 5.8 SO_2 Effect on NO Removal in Pilot Packed Scrubber ($\text{NaClO}_2 = 0.1 \text{ M}$, $\text{pH} = 7$, $\text{LFR} = 7 \text{ GPM}$).

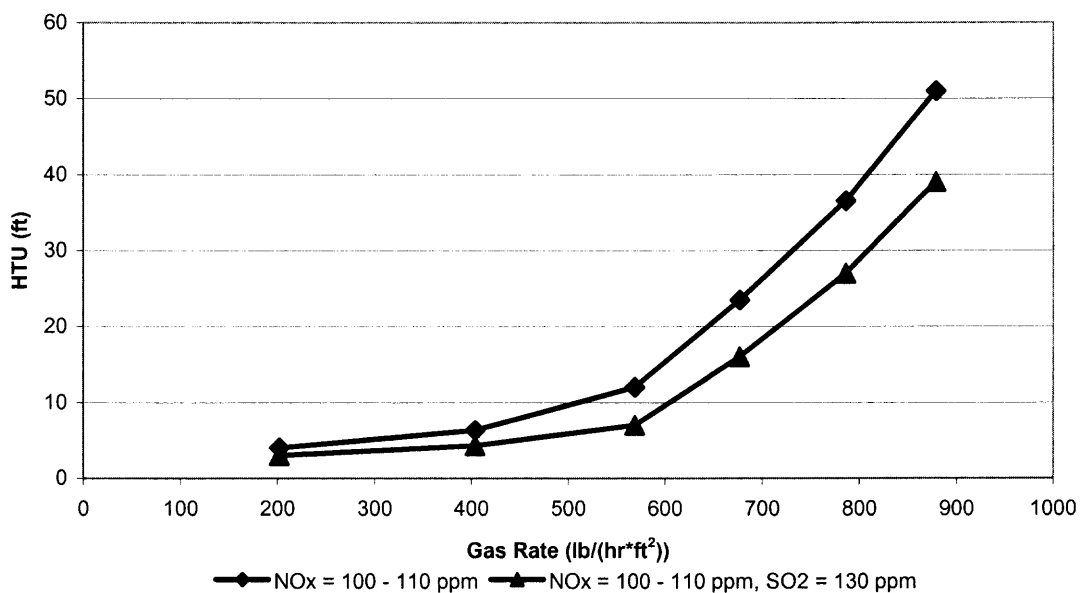


Figure 5.9 SO_2 Effect on NO_x Removal in Pilot Packed Scrubber ($\text{NaClO}_2 = 0.1 \text{ M}$, $\text{pH} = 7$, $\text{LFR} = 7 \text{ GPM}$).

In the model (equation 3.5) of calculation of HTU and K_{ga} for the packed bed NOx scrubbing with NaClO_2 , the equilibrium partial pressure is considered zero from the assumption of essentially irreversible and very fast reaction between NOx and NaClO_2 . Tests were conducted to check the correctness of the assumption with varying height of Glitsch grid packing. HTU were calculated using the equation (3.5) for 2 feet and 5 feet Glitsch grid packing heights. The results, Figure 5.10 and 5.11, show that calculated HTUs for the different packing heights match very well at lower gas flow rate. Certain error exists in the higher gas flow rates, because other system or instrumental errors have much more effect on HTU calculations with lower removal efficiencies than with higher removal efficiencies.

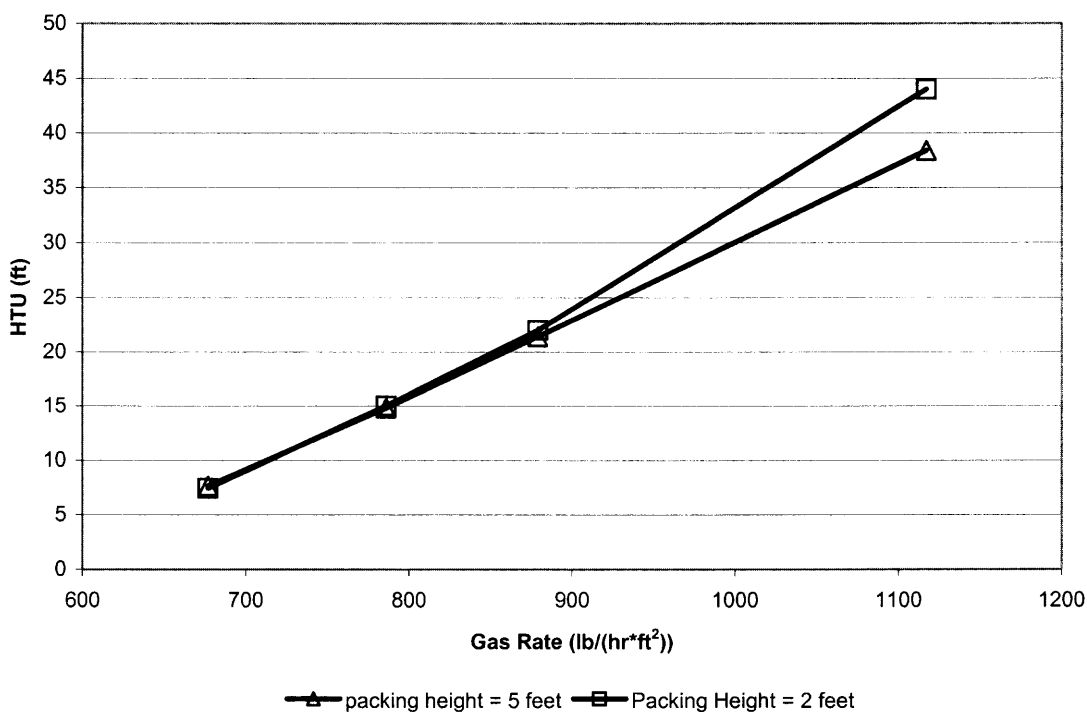


Figure 5.10 HTU Comparison on NO Removal in Pilot Packed Scrubber ($\text{NaClO}_2 = 0.1$ M, pH = 8, LFR = 7 GPM).

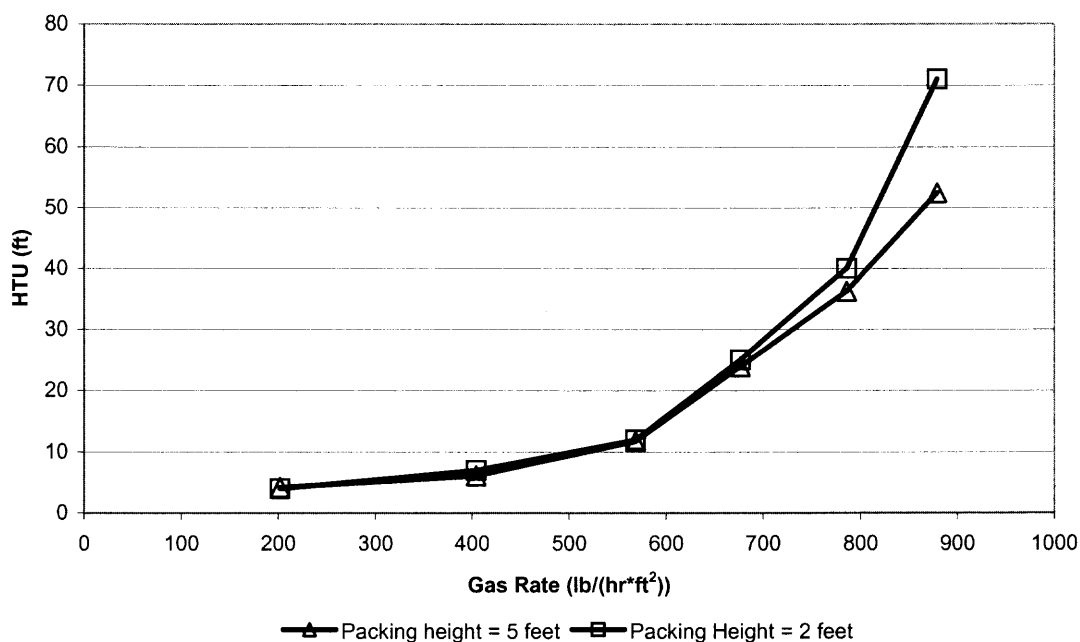


Figure 5.11 HTU Comparison on NO_x Removal in Pilot Packed Scrubber (NaClO₂ = 0.1 M, pH = 8, LFR = 7 GPM).

5.2.2 Pilot-Scale Mist Spray Scrubber

The Glitsch grid packing was removed from the tower and the spray tree was installed. A couple of tests were conducted under this set-up.

In a counter-current spray tower, drops of liquid are introduced by spray nozzles and are allowed to fall downward through a rising stream of flue gas. Spray tower is normally used for particulate collection. However, it can also be used as a gaseous pollutants absorption chamber. Its attractiveness stems from its low cost and simplicity, along with the capacity to handle particulate-laden gases due to its low pressure drop ^[35, 36]. Figure 5.12 is the pressure drop comparison between our packed bed and mist spray system. Contrary to the general belief that the spray tower has lower contact efficiency, it is almost as efficient as the packed bed tower under similar operating conditions.

Figure 5.13 indicates that the volumetric mass transfer coefficients firstly increase with the gas rates, then decrease abruptly after a certain point. The increase of $K_g a$ is resulted from the increased internal circulation motion of the droplets at higher gas velocity. The internal circulation is generally assumed to cause thinning of the outside boundary layer and thereby increasing the mass transfer rate between the gas phase and the drop. With further increase of gas rate, the upward velocity of the gas stream is greater than the falling speed of the droplet, which starts the entrainment of the droplets and thus decreases the mass transfer rate appreciably.

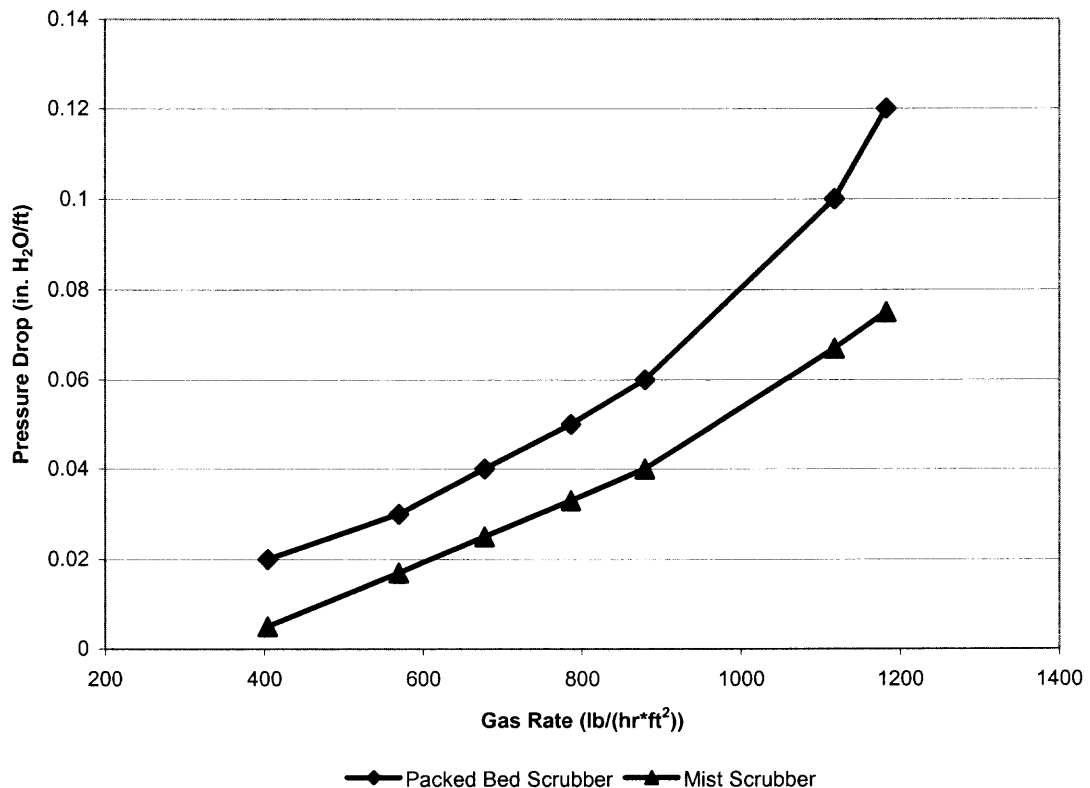


Figure 5.12 Pressure Drop Comparison (LFR = 6.5 GPM).

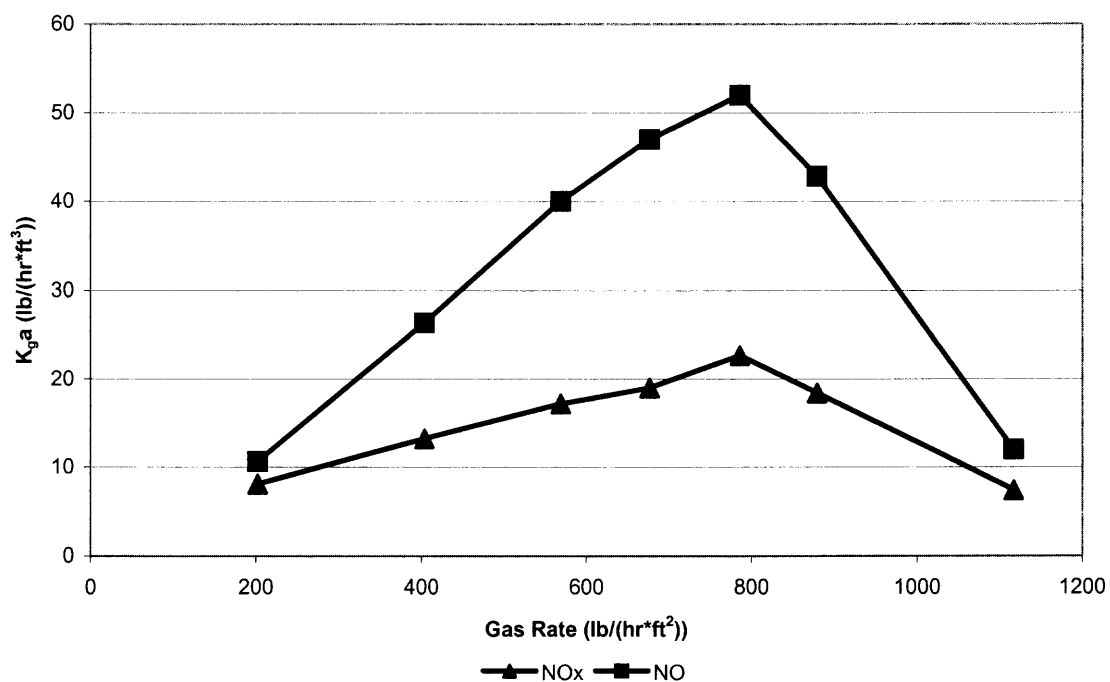


Figure 5.13 K_{ga} vs. Gas Rate in Mist Scrubber (NaClO₂ = 0.06 M, pH = 8, LFR = 6.5 GPM).

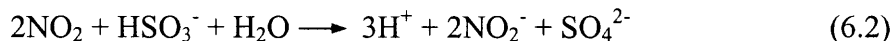
CHAPTER 6

OXIDATION OF AQUEOUS SULFITE ION BY NITROGEN DIOXIDE

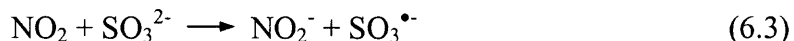
The bench-scale and pilot-scale NO_x scrubbing with NaClO₂ solutions shows that NaClO₂ is more effective on NO oxidation and NO₂ breakthrough is always observed in the outlet flue gas. Therefore, the development of a two-stage chemical scrubber for NO_x control might be necessary for more and more stringent environmental regulations and achieving zero emission of NO_x. The first stage would involve the NO oxidation to NO₂ using NaClO₂ accompanied by NO₂ oxidation and absorption into the solution. In the second stage, the remaining NO₂ from the first stage would be fully absorbed into the scrubbing liquid. The process especially designed for NO₂ removal may also find applications in the treatment of flue gases which have more NO₂ than NO, such as in the case of seven-hearth incinerator ^[43].

The sodium sulfite (Na₂SO₃) aqueous solution is found to be effective for NO₂ removal in a packed bed scrubber. NO₂ absorption occurs with simultaneous mass transfer and fast chemical reaction. Pilot-scale tests by Chen et al. ^[44] showed that at a sulfite concentration of 0.25 M and a gas-liquid contact time of 1.5 seconds, NO₂ absorption was more than 99%. The presence of Na₂SO₃ creates an irreversible reaction to drive NO₂ to the scrubbing solution.

There have been a number of studies of the reaction of nitrogen dioxide with sulfite in aqueous solution. However, the agreement between these studies is not always good, and some of the details of the reaction have not been established. Clifton and Altstein ^[45] proposed that the reaction proceeds via one or more intermediates to form nitrite and sulfate ions and the overall reaction appears to be:

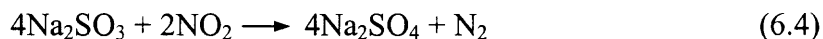


Littlejohn, Wang and Chang ^[46] believe that the reaction initially produce nitrite ion and sulfite radical ion:



Then the sulfite radical ion undergoes either recombination to form dithionate ion ($\text{S}_2\text{O}_4^{2-}$) in the absence of oxygen or reaction with oxygen to form sulfate.

Chironna and Altshuler ^[47] suggested that the main reaction that occurs when a large excess of SO_3^{2-} is present could be shown as:



The objective of this part of the work is to identify the products formed by the reaction of NO_2 and sulfite in aqueous solutions. Then, the material balance will be enclosed to ascertain the chemistry of the reaction.

6.1 Experimental

The reaction was investigated by flowing a gas mixture containing nitrogen dioxide through aqueous sodium sulfite solutions in a scrubber. The experimental apparatus consists of a flue gas blending system, a gas scrubber and an analytical train. Figure 6.1 presents the schematic of the experimental system. The blending system is capable of producing a mixture of helium, oxygen, nitrogen dioxide at different concentrations. A bubble column is used as the scrubber. The effluent gases were continuously measured by a Nicolet 520 FTIR for NO , NO_2 and N_2O analysis, and a Hewlett Packard 5890A Gas

Chromatography for N_2 detection. After each experiment, liquid samples were removed to measure the anion concentrations in the solution in a Waters Ion Chromatograph.

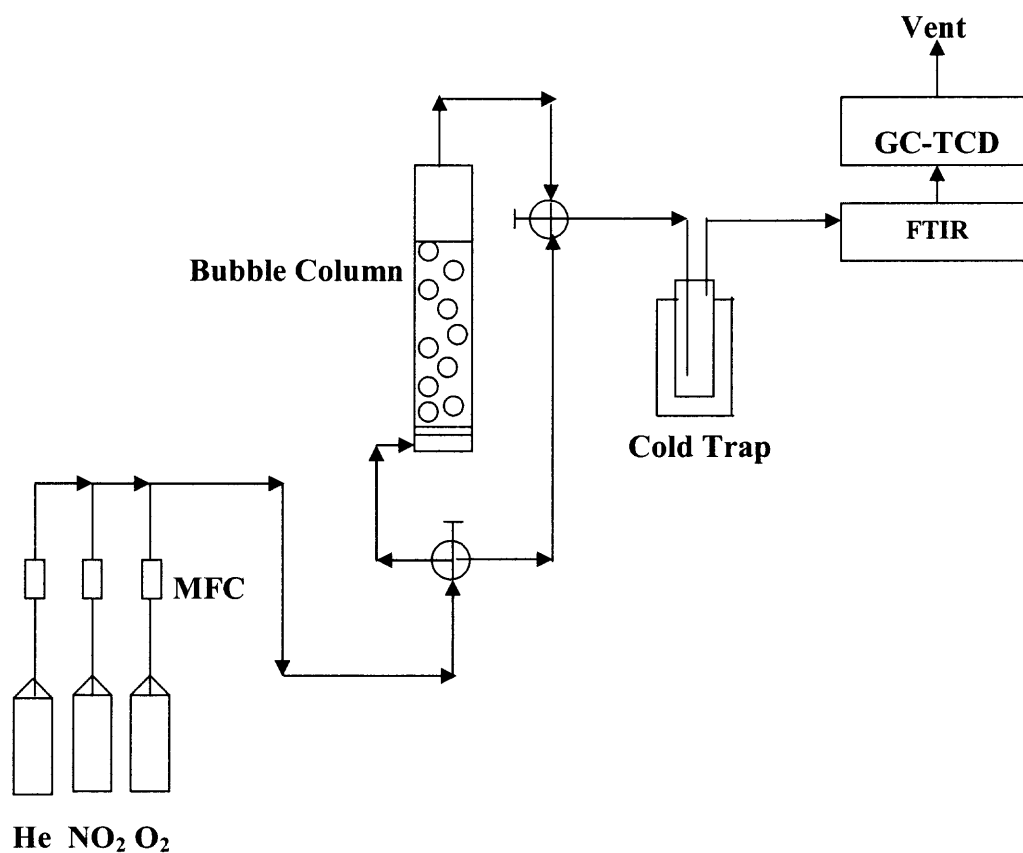


Figure 6.1 Schematic Diagram of Laboratory Apparatus to Study NO_2 Reaction with Aqueous Sulfite Ion.

6.1.1 Scrubbing Vessel

The flue gas scrubber is a 4.2 cm diameter by 14.5 cm long Pyrex glass column with a sparger located at the bottom. The flue gas is introduced into the scrubbing solution through the sparger as illustrated in Figure 6.1.

One hundred and sixty milliliters of Na_2SO_3 solution was used to run semi-batch experiments with continuous injection of gas. The existing gas is carried to the analyzers

from the top of the glass column after moisture condensation at 0°C. Liquid samples are analyzed with IC after each run.

6.1.2 Gas Analysis

The inlet and outlet gas compositions are analyzed continuously by FTIR and Gas Chromatography with a thermal conductivity detector (GC-TCD).

A Nicolet 520 FTIR equipped with a 2 m gas cell is used to measure the concentration of NO, NO₂ and N₂O. The instrument is calibrated with certified gaseous mixtures in which helium is the balance gas. At least three different mixtures in the range of interest are used to obtain the overall calibration curve. The FTIR is used in a scanning mode of 20 scans per sample.

A Hewlett Packard 5890A Gas Chromatograph with thermal conductivity detector is connected after the FTIR to detect any nitrogen that may have been produced during the absorption of NO₂. The column used for the GC is 0.32 cm in diameter by 9.14 m long stainless steel column packed with 100/120 mesh HayeSep DB. The operating conditions for the GC-TCD are summarized below:

- Oven Temperature 0°C
- Injection Temperature 80°C
- Detector Temperature 140°C
- Carrier Gas He

The detection limit of this method was reported to be 4.05 mg/m³ nitrogen (3.24 ppmv nitrogen) ^[48].

It should be noted that for the purpose of these experiments, the nitrogen gas which is present as the major component from combustion system effluents has been replaced by Helium gas for two reasons:

- (1) Since we are trying to determine if N_2 is produced from the absorption of NO in SO_3^{2-} , the small quantity of N_2 so produced would be difficult to measure by difference if N_2 were used as balance gas.
- (2) Helium has been chosen as the replacement gas to N_2 because the thermal conductivity difference between N_2 and He is very large and will give us a more accurate measurement of any N_2 produced.

6.1.3 Scrubbing Solution Analysis

A Waters ion chromatography equipped with a Waters 715 Ultra WISP Sample Processor, a Waters 484 Tunable Absorbance Detector and a Waters 431 Conductivity Detector was used to analyze the anions in the scrubbing solutions. The column used for the IC is IC-Pak Anion HC. The eluent (mobile phase) for the analysis is Borate/Gluconate with a flow rate of $2 \text{ cm}^3/\text{min}$. A Guard-Pak Precolumn Cartridge: IC-PAK Anion, is installed before the separation column to protect the column, and a solid phase chemical suppressor cartridge (SPCS) is installed after the separation column and before the conductivity detector. The UV detector was set at 214 nm to detect nitrate and nitrite ions.

Calibration curves for nitrite, and nitrate, and sulfate are shown in Figure 6.2, 6.3, and 6.4 respectively. The retention times for the sodium salts of NO_2^- , NO_3^- , and SO_4^{2-} are 6.2, 9.6, and 16.5 min, respectively. The detection limits for NO_2^- , NO_3^- , and SO_4^{2-} are 3.0, 5.2, and 9.1 ppb respectively.

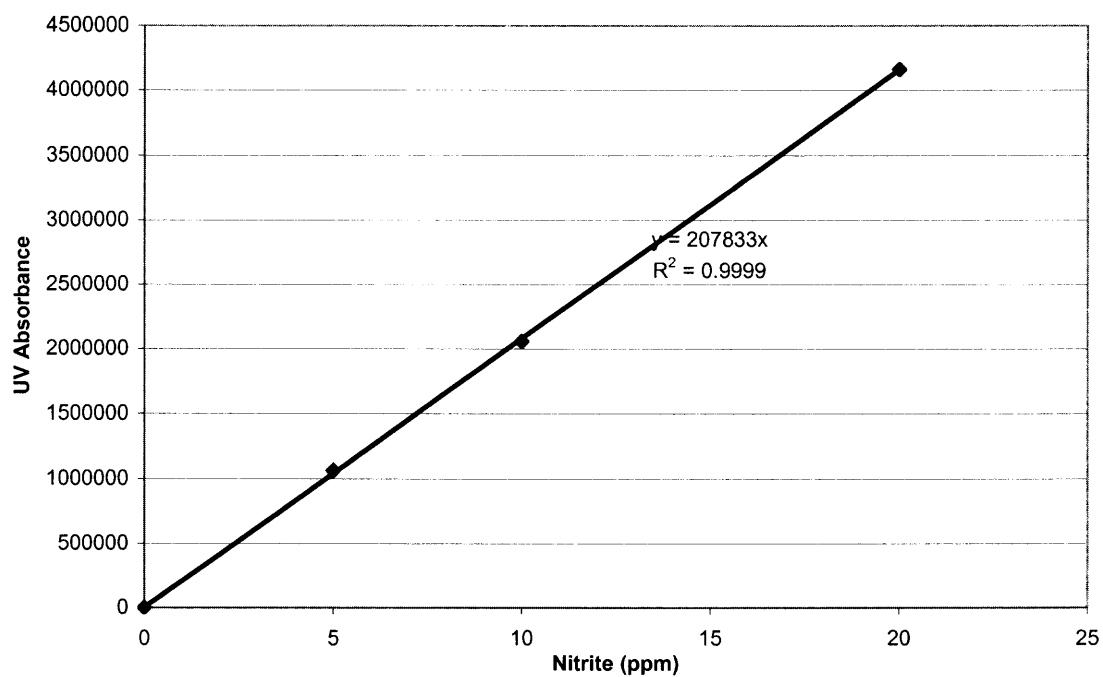


Figure 6.2 Calibration Curve for Nitrite (UV Detector).

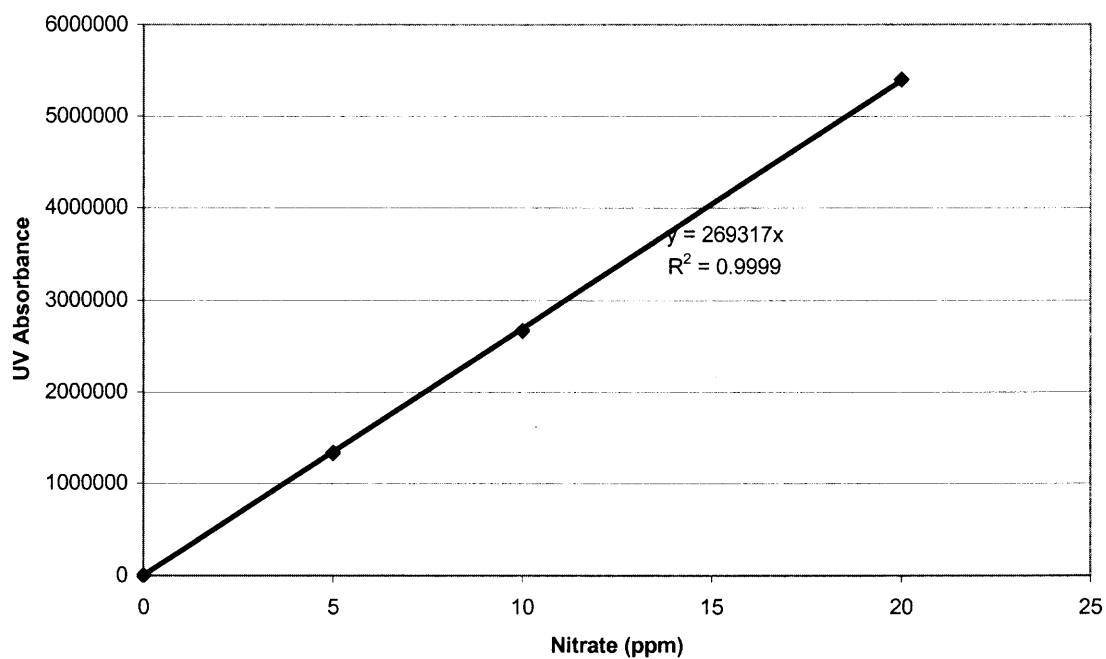


Figure 6.3 Calibration Curve for Nitrate (UV Detector).

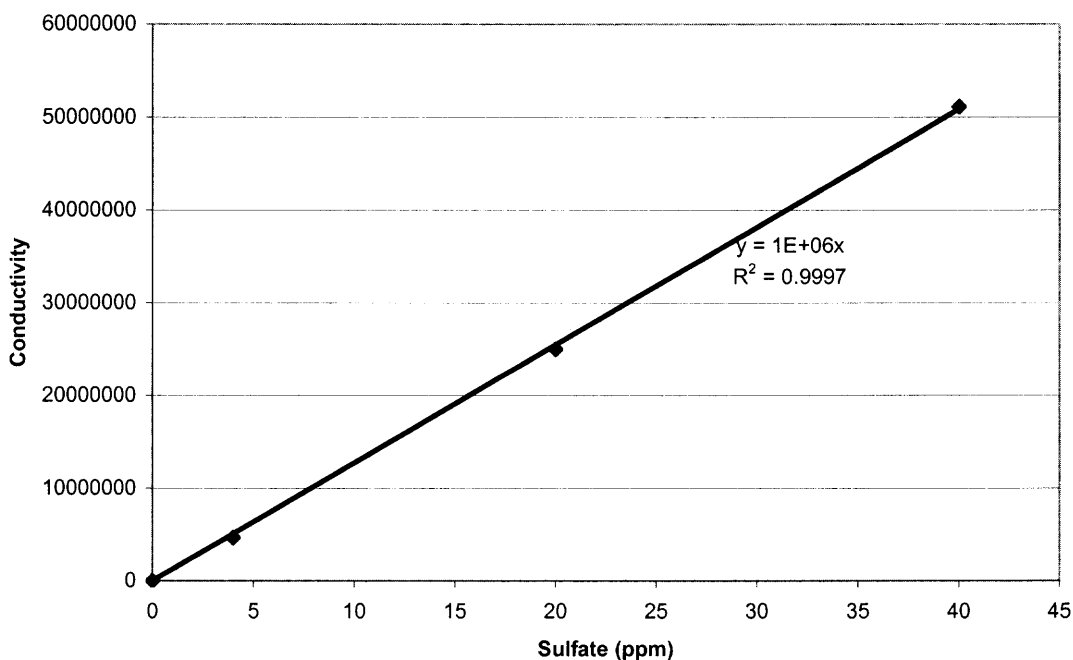


Figure 6.4 Calibration Curve for Sulfate (Conductivity Detector).

6.2 Results and Discussion

The products and nitrogen balance of the reaction of NO_2 with sulfite ion were determined both in the presence and in the absence of gaseous oxygen.

6.2.1 NO_2 Reaction with Sulfite in the Absence of Oxygen

The conditions selected for this experiment are outlined below:

- Scrubbing solution: 160 ml of 0.25 M aqueous Na_2SO_3 solution
- Flue gas composition: 1050 ppm NO_2 in He
- Flue gas flow rate: 300 – 500 cm^3/min
- Scrubbing temperature: room temperature
- Running time: 1.5 – 2.5 hours

Before each experiment, the whole system was purged with pure helium to remove all the air present in the system. After 30 minutes of purging, a GC measurement was made as a background for N_2 detection. Then the He was closed while the synthetic flue gas was allowed to flow through the scrubbing system.

The results from the FTIR showed that no NO_2 breakthrough occurred, and neither N_2O nor NO was observed. Similarly, no N_2 was found using the GC method.

Results of the nitrogen balance of the reaction in the absence of oxygen are given below in Table 6.1 – 6.3.

Table 6.1 Nitrogen Balance for NO_2 Reaction with Aqueous Sulfite Ion in the Absence of O_2 (Experiment No. 1)

Source	Compound	Initial Amount (Moles)	Final Amount (Moles)	Percentage of Final Amount in Total Initial Amount (%)
Gas	NO_2	0.00115	-	-
Gas	NO	-	-	-
Gas	N_2	-	-	-
Gas	N_2O	-	-	-
Aqueous	NO_2^-	-	0.000515	44.8
Aqueous	NO_3^-	-	0.000031	2.7
	Total	0.00115	0.000546	47.5

Table 6.2 Nitrogen Balance for NO_2 Reaction with Aqueous Sulfite Ion in the Absence of O_2 (Experiment No. 2)

Source	Compound	Initial Amount (Moles)	Final Amount (Moles)	Percentage of Final Amount in Total Initial Amount (%)
Gas	NO_2	0.00172	-	-
Gas	NO	-	-	-
Gas	N_2	-	-	-
Gas	N_2O	-	-	-
Aqueous	NO_2^-	-	0.000831	48.3
Aqueous	NO_3^-	-	0.000031	1.8
	Total	0.00172	0.000862	50.1

Table 6.3 Nitrogen Balance for NO₂ Reaction with Aqueous Sulfite Ion in the Absence of O₂ (Experiment No. 3)

Source	Compound	Initial Amount (Moles)	Final Amount (Moles)	Percentage of Final Amount in Total Initial Amount (%)
Gas	NO ₂	0.00215	-	-
Gas	NO	-	-	-
Gas	N ₂	-	-	-
Gas	N ₂ O	-	-	-
Aqueous	NO ₂ ⁻	-	0.001017	47.3
Aqueous	NO ₃ ⁻	-	0.000008	0.4
	Total	0.00215	0.001025	47.7

From the data above, it appears that no nitrogen is produced in the reaction, and approximately 50% of absorbed NO₂ is recovered by IC in the absence of oxygen, in which nitrite ion is the main component with trace amount of nitrate ion. It is likely that some other nitrogen containing products are also produced during the reaction, but due to the limitation of the IC column being used, they were not detected.

6.2.2 NO₂ Reaction with Sulfite in the Presence of Oxygen

The conditions selected for this experiment are outlined below:

- Scrubbing solution: 160 ml of 0.25 M aqueous Na₂SO₃ solution
- Flue gas composition: 500 ppm NO₂ in He
0.05% O₂ in He
- Flue gas flow rate: 300 – 500 cm³/min
- Scrubbing temperature: room temperature
- Running time: 1 – 2 hours

The results from the FTIR showed that no NO₂ breakthrough occurred, and neither N₂O nor NO was observed. Similarly, no N₂ was found using the GC method.

Results of the nitrogen balance of the reaction in the presence of O₂ are given in

Table 6.4 – 6.6.

Table 6.4 Nitrogen Balance for NO₂ Reaction with Aqueous Sulfite Ion in the Presence of O₂ (Experiment No. 1)

Source	Compound	Initial Amount (Moles)	Final Amount (Moles)	Percentage of Final Amount in Total Initial Amount (%)
Gas	NO ₂	0.000471	-	-
Gas	NO	-	-	-
Gas	N ₂	-	-	-
Gas	N ₂ O	-	-	-
Aqueous	NO ₂ ⁻	-	0.000346	73.5
Aqueous	NO ₃ ⁻	-	0.000062	13.2
	Total	0.000471	0.000408	86.7

Table 6.5 Nitrogen Balance for NO₂ Reaction with Aqueous Sulfite Ion in the Presence of O₂ (Experiment No. 2)

Source	Compound	Initial Amount (Moles)	Final Amount (Moles)	Percentage of Final Amount in Total Initial Amount(%)
Gas	NO ₂	0.000901	-	-
Gas	NO	-	-	-
Gas	N ₂	-	-	-
Gas	N ₂ O	-	-	-
Aqueous	NO ₂ ⁻	-	0.000751	83.4
Aqueous	NO ₃ ⁻	-	0.000051	5.7
	Total	0.000901	0.000802	89.1

Table 6.6 Nitrogen Balance for NO₂ Reaction with Aqueous Sulfite Ion in the Presence of O₂ (Experiment No. 3)

Source	Compound	Initial Amount (Moles)	Final Amount (Moles)	Percentage of Final Amount In Total Initial Amount (%)
Gas	NO ₂	0.000692	-	-
Gas	NO	-	-	-
Gas	N ₂	-	-	-
Gas	N ₂ O	-	-	-
Aqueous	NO ₂ ⁻	-	0.000561	81.1
Aqueous	NO ₃ ⁻	-	0.000074	10.7
	Total	0.000692	0.000635	91.8

From the data above, it is clear that no nitrogen gas is produced in the reaction, and over 85% of absorbed NO_2 is found by IC in the presence of oxygen, in which nitrite ion is the principal product with a small quantity of nitrate ion.

The comparison between the reaction with and without O_2 presence showed that O_2 plays an important role in the reduction of NO_2 . The higher recovery rate with O_2 presence indicated the existence of some intermediate nitrogen products, which can react with O_2 to form NO_2^- and NO_3^- .

CHAPTER 7

CONCLUSIONS

The oxidation and absorption of NO_x from a fluid catalytic cracking regenerator effluent gas using aqueous sodium chlorite solutions was studied in bench-scale packed bed scrubber, bench-scale ejector Venturi scrubber, and pilot-scale packed bed and mist spray scrubbers. Up to 100% of NO and 90% of NO_x can be removed by the systems. Also, a simultaneous removal of SO₂ was always achieved. NO_x removal increases with increasing NaClO₂ concentration, temperature, acidity of the solution, and residence time. The NO and NO_x removal are significantly affected by the gas rate with low concentration of NaClO₂ in the pilot system. In the operating range studied in the pilot system, NaClO₂ concentration of 0.1 M or above is necessary for effective removal of NO_x. The existence of SO₂ in the flue gas greatly increases the reaction rate of NO_x with NaClO₂. The tests on lower NO_x inlet concentration indicate that these systems are also effective for NO_x control after a Thermal DeNO_x pretreatment. The pH of the scrubbing solutions from 6 to 7 is ideal for this practice due to its acceptable NO_x removal efficiencies, no absorption of CO₂ into the solutions, low level of corrosion to the equipment, and the ability to remove NH₃ in the same system. The generation of smaller amount of nitrate and nitrite in the spent solutions with a lower NO_x inlet concentration and the advantage of removing all the pollutants, NO_x, SO₂, particulates and NH₃, in the same system make the combination of Thermal DeNO_x and wet scrubbing with aqueous NaClO₂ solutions very unique and attractive to treat FCC regenerator flue gases. Contrary to the general belief of lower contact efficiency of the spray tower, the spray tower is almost as efficient as the packed bed tower for NO removal. The low cost spray

tower can be used as the first stage scrubber in the two-stage NO_x control system for transform NO to NO₂, and then NO₂ can be fully scrubbed by a sulfite system.

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