

**CHAPTER 2:
LITERATURE REVIEW**

2.1 Nitrogen Oxides in the Environment

2.1.1 Hazards Associated with Nitrogen Oxide Compounds in the Environment

Nitrogen oxide (NO_x) gases are widely accepted to be harmful entities in the environment. NO_x gases in their incipient emission forms are generally poisonous to humans and animals. NO_x gases also contribute to smog, ozone depletion, and acid rain. As a result of chemical reactions with other atmospheric components, various NO_x gases transform into the components for smog and acid rain. Smog forms as a result of the reaction of NO₂ with airborne particulates in a photochemical process. Acid rain forms when NO₂ absorbs into water vapor in the atmosphere. NO_x gases, however, do not linger in the atmosphere for long periods of time. They steadily proceed through a cycle of harmful intermediates, do their damage, and are cleared from the atmosphere by precipitation and wind dispersion.

The harmful effects of NO_x gases are typically centered in dense industrial and urban areas where production of NO_x gases from industry or automobiles exceed neutralization and dispersion forces. NO_x also accumulates where the normal factors of wind and precipitation are hindered by geography, e.g. the Los Angeles valley. Nitric oxide, NO, transforms to nitrogen dioxide, NO₂, consuming ozone in the process. However, nitrogen and oxygen do not readily form NO in the atmosphere because the reaction, $N_2 + O_2 \rightarrow 2NO$, has an extremely high activation energy. Even at elevated temperatures, equilibrium NO levels are low. Therefore, we know that man-made vehicles and factories represent the main source of NO in the atmosphere.

2.1.2 Sources of NO_x Gases Released to the Environment

Combustion processes that raise air temperatures to conditions where the reaction, $N_2 + O_2 \rightarrow 2NO$, proceeds at an appreciable rate represent a major source of NO_x gases released to the atmosphere. Mobile sources like automobiles release NO_x gases in their exhaust. Stationary sources, such as coal-burning power plants, produce NO_x gases both from the reaction of nitrogen and oxygen in heated air feed, as well as the oxidation of nitrogenous compounds embedded in the coal. Non-combustion sources also contribute a lesser, although appreciable,

amount of NO_x gases. Table 2.1 shows that the predominant NO_x species emitted from stationary sources is NO. Of these major contributors, nitric acid plants contribute the most NO₂ to the environment.

Table 2.1. List of types of stationary sources and their primary NO_x species emitted (Cheremisinoff and Young, 1977).

Stationary source	Major component
Electrical power plants	NO
Industrial combustion sources	NO
Stationary industrial combustion engines used in pipe lines and gas plants	NO
Domestic and commercial combustion equipment	NO
Nitric acid plants	NO₂

Combustion sources generally have NO as the main component of NO_x pollution. NO subsequently transforms to NO₂ in the atmosphere after emission, and thus we still consider these plants to be NO₂ sources. However, NO dominates the NO_x at the point of potential treatment, that of the immediate emission. We must consider this fact in attempts to treat such emissions, because NO treatment differs from treatment for NO₂ as well as that for mixtures of NO and NO₂. Nitric acid plants and others operating an ammonia oxidation process or some other use of nitric acid generally have NO₂ as their major component of NO_x gas emissions. This fact follows from the objective of the ammonia oxidation plant to supply NO_x at as high an oxidation state as possible for subsequent conversion to HNO₃. For this reason, and the fact that their emissions are usually of a much lower temperature than that of combustion sources, nitric acid plants require a different approach to flue-gas treatment.

2.2 Various NO_x Control Techniques for Flue-Gas Emissions from Stationary Sources

Traditionally, NO_x has been one of the most expensive and difficult pollutants to control. This fact, plus the complexity of NO_x chemistry, has kept the number of sites using old technology to reduce NO_x emissions to very few. Relatively new evidence of the detrimental effects of fugitive NO_x in the environment and the subsequent environmental protection regulations have necessitated the development and implementation of new technologies to improve the effectiveness and economics of NO_x control efforts. The highly concentrated industrial centers in Japan have been the world's largest application areas for NO_x control. Thus, the Japanese developed most of the newer techniques for NO_x control. The prospect of even tougher restrictions gives priority to the development of processes that have good performance as well as adequate room for growth and improvement.

The most obvious, first approach to NO_x control is that of reducing the initial production and liberation of NO_x gases. In combustion processes, this approach takes many forms. Process design minimizes the opportunity for NO_x-producing pathways. More stringent process control tightens sloppy processes for which NO_x is a side-reaction product. Equipment-design changes minimize the variables that are most favorable to NO_x formation.

In combustion of hydrocarbon fuels, NO_x emerges as an unfortunate by-product. Oftentimes, NO_x can be reduced in the source through some of the aforementioned techniques. In ammonia oxidation, for nitric acid production and other purposes, NO_x is ironically the intended product. Not only are no attempts made to reduce NO_x production, nitric acid plants focus great effort on maximizing NO_x production. However, these plants still aim to minimize the release of NO_x to the atmosphere, because NO_x not only constitutes a controlled fugitive emission but also the valuable product. For this case, and others where process modifications do not sufficiently reduce NO_x destined for emission, flue-gas treatment for NO_x reduction is necessary to comply with regulation levels of NO_x released. There are mainly two types of flue-gas treatment methods: wet and dry processes.

2.2.1 Wet Processes

We limit our discussion to two processes relevant to the objectives of this work. First, we discuss the specific wet scrubbing approach known as the sodium acetate process. Next, we introduce extended absorption, which we discuss in greater detail later in this thesis.

2.2.1.1 Wet Scrubbing

The wet processes involve absorption and subsequent reaction of NO_x in the aqueous phase. Direct absorption involves a reaction chain that achieves both SO_x and NO_x removal. One form involves an SO₂ reaction step, a subsequent NO reaction, and a termination step that produces gypsum. Table 2.2 shows the different steps involved in the process.

The advantage of these processes is their ability to eliminate gaseous NO_x and SO_x simultaneously. However, this fact represents a disadvantage for processes that do not produce SO_x in adequate quantities to maintain the chain-reaction mechanism. Also, this process turns an air-pollution problem into a wastewater problem. Figure 2.1 shows a proposed flowsheet for the direct absorption process.

Table 2.2. Reaction steps and pathway equations for the sodium acetate direct absorption process for simultaneous NO_x and SO_x removal (OECD, 1983).

Absorption and gypsum formation
<p>Absorption</p> $\text{SO}_2 + 2\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_3 + 2\text{CH}_3\text{COOH}$ $2\text{NO} + 5\text{Na}_2\text{SO}_3 + 4\text{CH}_3\text{COOH} \rightarrow 2\text{NH}(\text{NaSO}_3)_2 + \text{Na}_2\text{SO}_4 + 4\text{CH}_3\text{COONa} + \text{H}_2\text{O}$
Gypsum formation
$\text{Na}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 + 2\text{CH}_3\text{COOH} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{CH}_3\text{COONa}$
Imide treatment step
<p>Hydrolysis</p> $\text{NH}(\text{NaSO}_3)_2 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 + \text{Na}_2\text{SO}_4$ <p>Release of NH₃</p> $\text{NH}_4\text{HSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{NH}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ <p>Nitrogen gas formation</p> $4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$

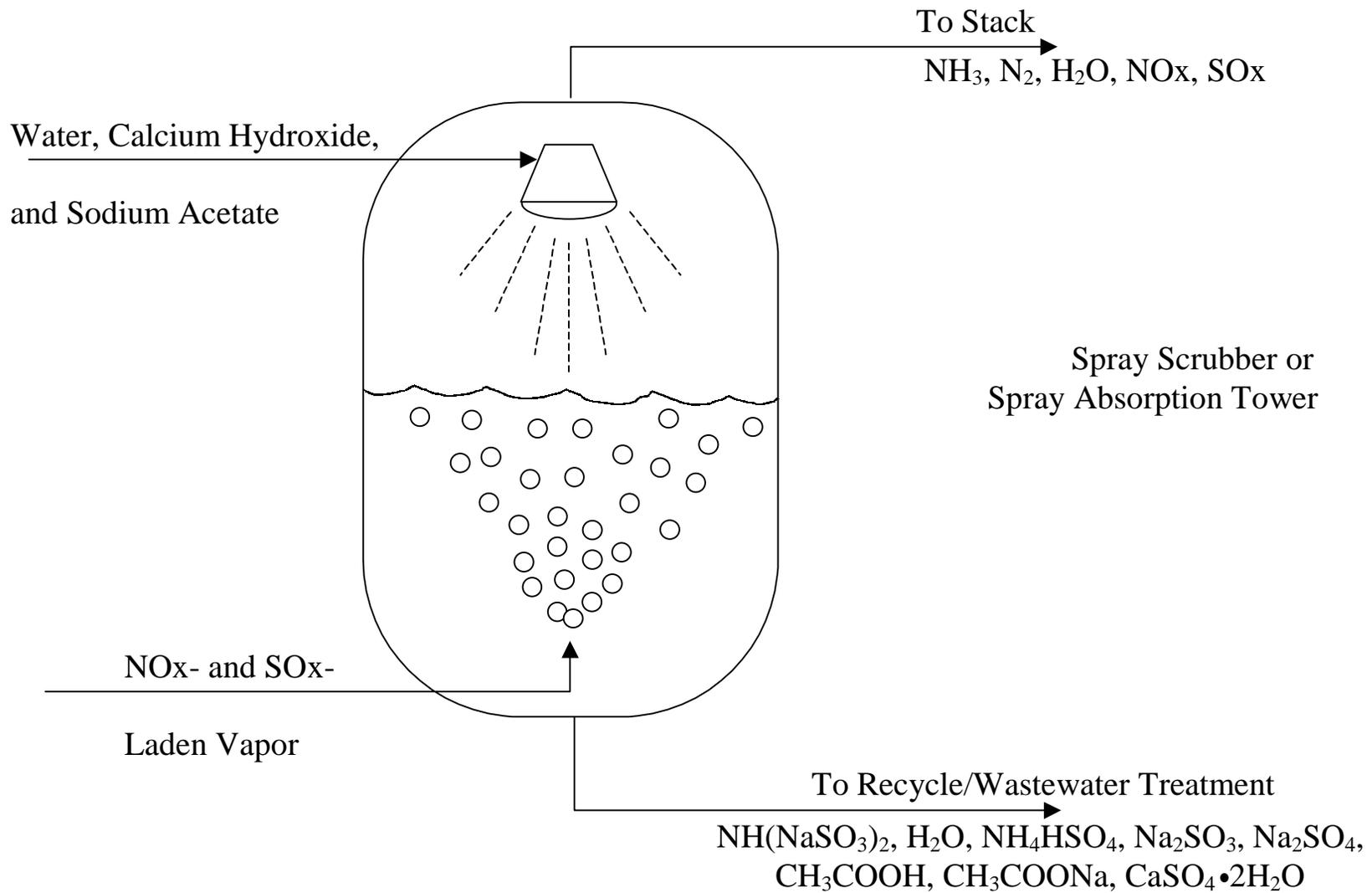


Figure 2.1. Flowsheet for a wet scrubbing process involving simultaneous removal of SO_x and NO_x.

2.2.1.2 Extended Absorption

Nitric acid manufacture presents the most logical opportunity for implementing extended absorption. Extended absorption involves the addition of one or more absorption towers to an existing absorption system. An ammonia oxidation process produces NO_x gases in most existing nitric acid plants. The existing absorption system at such plants absorbs NO_x from the off-gases from the ammonia-oxidation facility. Adding more absorption columns for these sites makes sense for several reasons. First, using a new column that is similar to those in place simplifies design and control strategies. The absorbed NO_x becomes nitric acid and contributes to the product, instead of the acidic wastewater problem for the site. Also, no arrangements for supplying reactants are required for other NO_x removal processes.

The relatively low solubility of NO_x gases in water represents the major problem with absorption. Given diminishing returns on absorption efforts, the emission problem remains if the extended absorption towers fail to bring NO_x gases to acceptable levels. Figure 2.2 shows how the extended absorption process fits into an existing nitric acid plant.

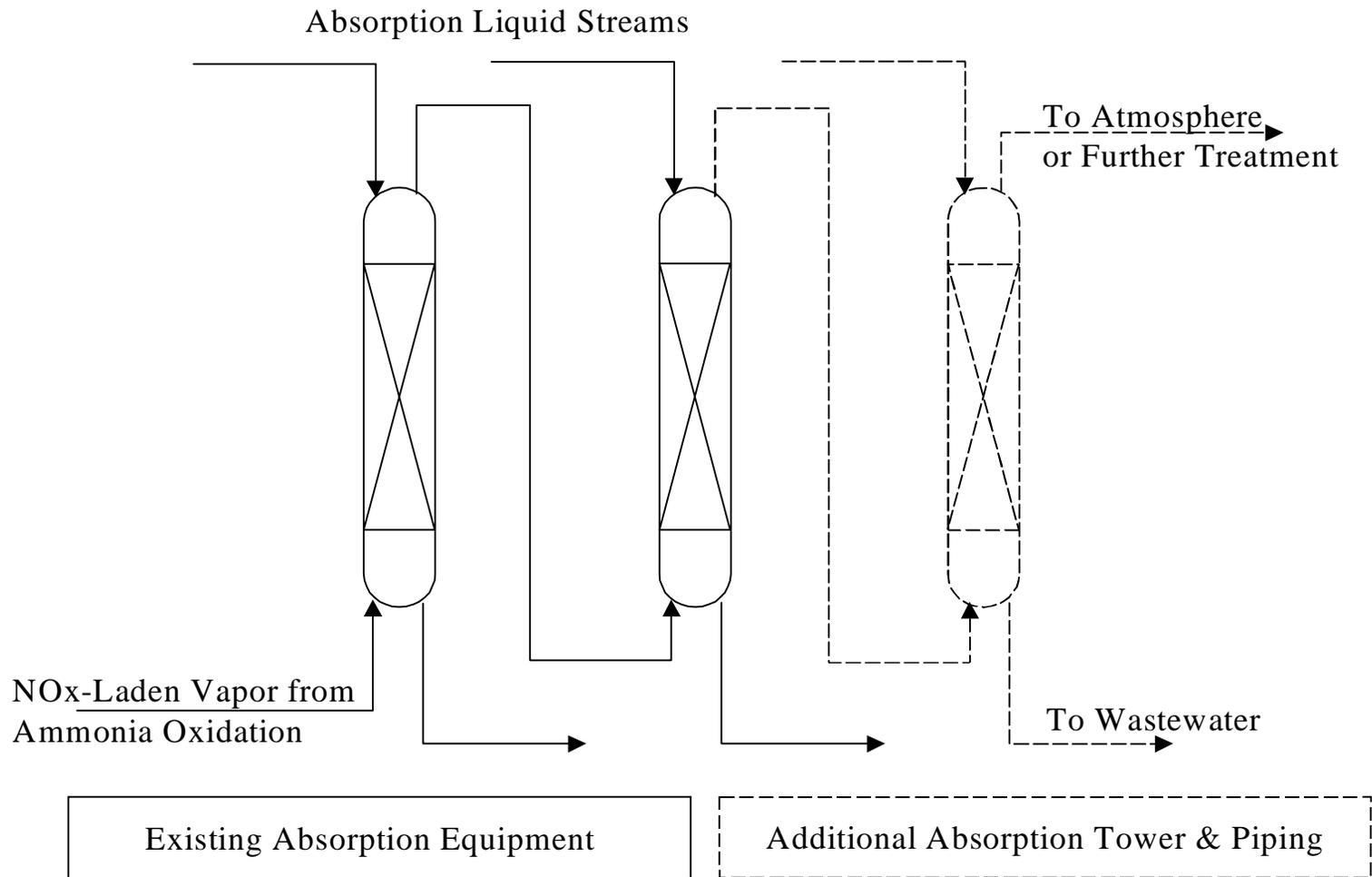


Figure 2.2. Flowsheet for extended absorption. An additional absorption tower and piping are added (shown dashed) to the existing equipment (solid lines).

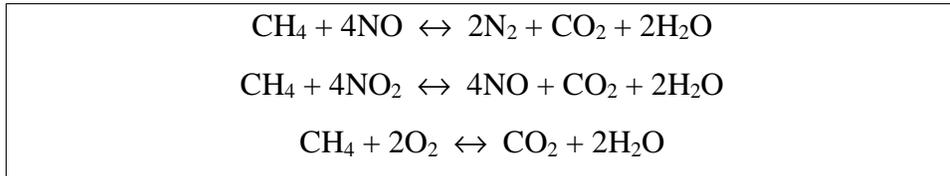
2.2.2 Dry Processes

Ease and flexibility of operation, recoverable heat generation, and high NO_x removal generally characterize the dry NO_x reduction processes. The processes are located in the flue-gas stream and can be used in conjunction with extended absorption processes upstream of the flue gas.

2.2.2.1 Non-Selective Catalytic Reduction (NSCR)

NSCR utilizes CH₄, CO, or H₂ to reduce NO_x and O₂ over a platinum or palladium catalyst bed. We call this type of process non-selective because of the preference of the fuels for the reduction of O₂ (oxidation of the fuels). The availability of natural gas as a source of CH₄ represents a clear advantage to this technique. Using natural gas as the reducing agent requires the stream to be heated to 900 °F (482 °C). Using H₂ requires a stream temperature of 300 °F (149 °C). Table 2.3 shows the most probable reactions when using CH₄ as the reducing agent.

Table 2.3. Reactions involved in the non-selective catalytic reduction of NO_x (OECD, 1983).



The oxidation of the fuel species also produces high levels of heat. The heat evolved maintains the reaction temperature in the catalyst vessel. Also, intelligent process-integration recovers the heat generated to supplement the utility duties of the plant.

NSCR cannot yield highly efficient NO_x removal. It gives a maximum NO_x removal of approximately 50%. In process situations where there is excess oxygen in the flue-gas stream, the fuel components will preferentially react with oxygen. This situation may prove prohibitive in the quantities of fuel required for consuming the NO_x gases. Also, oxygen reacting with the

reducing agent generates large quantities of heat. The temperature must be kept below the maximum for catalyst activity, and without heat recovery, this process is not economical compared to other dry processes. Figure 2.3 shows a typical flow scheme for the non-selective catalytic reduction process.

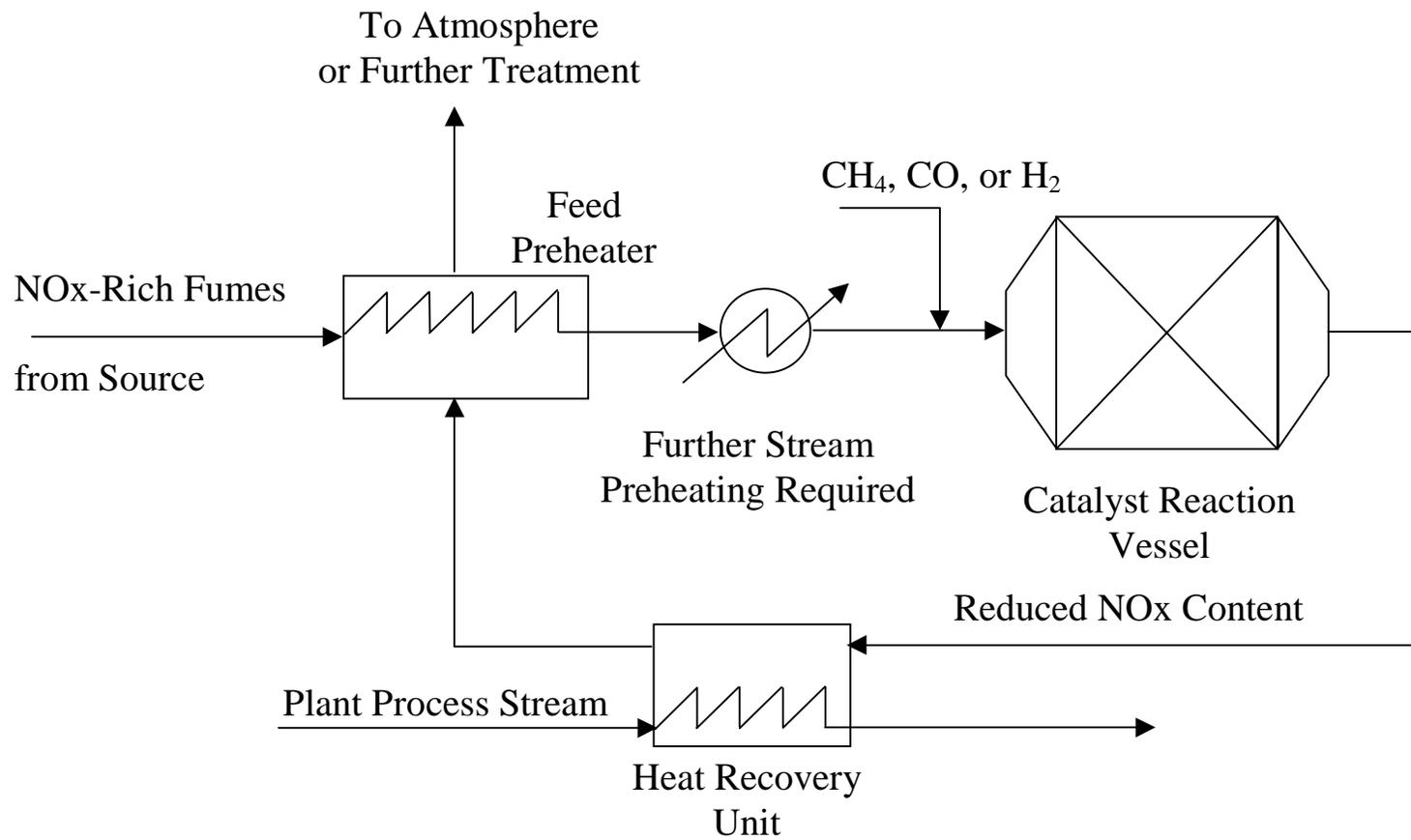


Figure 2.3. Flowsheet for a non-selective catalytic reduction (NSCR) process.

2.2.2.2 *Selective Catalytic Reduction (SCR)*

Selective catalytic reduction uses ammonia to reduce NO and NO₂ to N₂ over a catalyst bed. SCR can give NO_x removal of up to 90%. The reactions involved run at lower temperatures than those of non-selective catalytic reduction. Temperature control in this process is key. Too low of a temperature poses a threat of production of ammonium nitrates that can crystallize and build up in the stack. Too high of a temperature can cause the oxidation of NH₃ and the production of more NO_x gases. Ideally, the catalyst vessel temperature should be maintained between 572 °F (300 °C) and 752 °F (400 °C) (EPA Document 450383002). This temperature range makes major heat recovery unnecessary and unfeasible. We must also keep the temperature above a level favoring the production of ammonium-nitrate salts. These solids may build up in the flue system and pose an explosive hazard. Ammonia is readily available on a plant site that has an ammonia-oxidation process. However, the higher costs of the catalyst and the ammonia fuel increase the capital and operating costs of this process over the non-selective catalytic reduction.

The stoichiometric ratio of ammonia to NO_x must be kept at 1:1 to maximize NO_x removal and minimize the escape of unreacted NH₃ from the reactor. We refer to the NH₃ that exits in the reactor as ammonia (NH₃) slip. Loss of NH₃ in the flue creates another air-pollution problem as well as the loss of valuable reactant. Slippage of NH₃ also poses a danger of deposition of ammonium-nitrate formation in the flue gas as the stream cools. Figure 2.4 shows the piping and equipment layout for the SCR process.

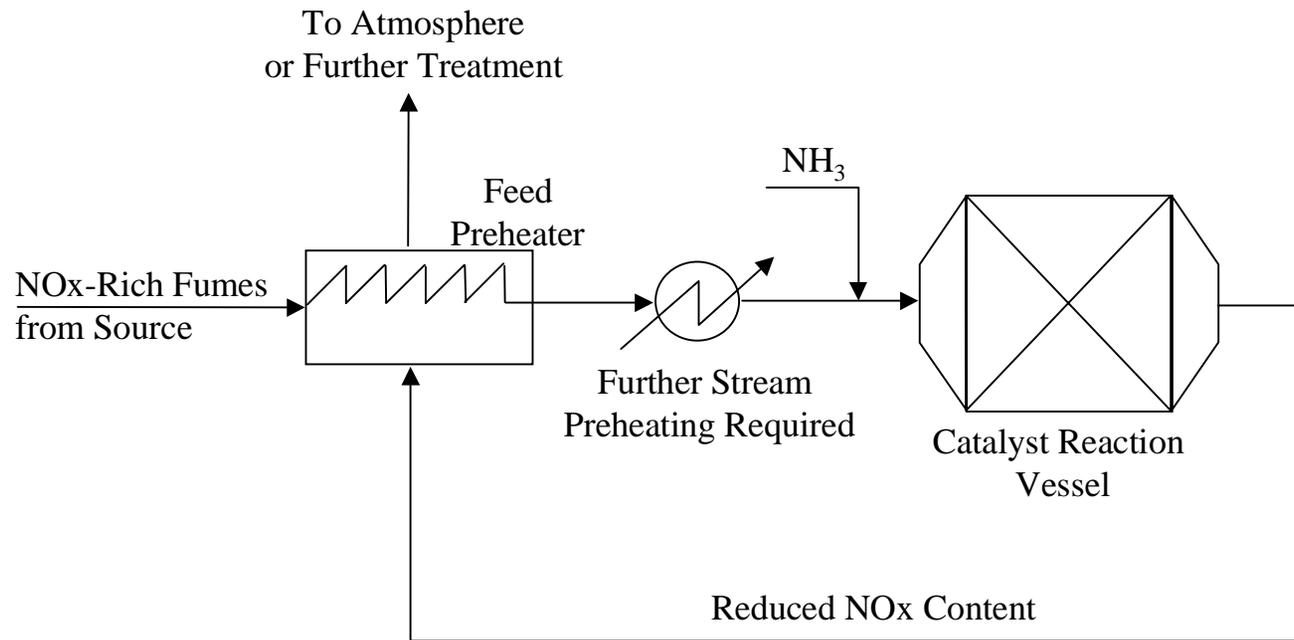


Figure 2.4. Flowsheet for a selective catalytic reduction (SCR) process.

As we state previously, NO makes up the main component of NO_x in gases produced at coal-burning and other combustion facilities. Nitric acid plants differ in that they produce NO₂ as the main component of effluent with NO mixed in to a lesser extent depending on process conditions. Most literature information focuses on dealing with gases containing NO. The literature contains little information on the subject of dealing with gases that contain a mixture of NO and NO₂ as is often the case at nitric acid plants. However, the presence of NO₂ provides the opportunity to link an SCR with a scrubber/absorber system, because NO₂ is soluble whereas NO is not.

2.2.2.3 Selective Non-Catalytic Reduction (SNCR)

Selective non-catalytic reduction uses urea or ammonia as the reducing agent for NO_x gases. Elevated temperatures allow for reaction in the absence of a catalyst. The elevated temperatures also tend to favor certain unwanted compounds, such as NO and N₂O, making this process less desirable than SCR. Figure 2.5 shows the flow scheme for selective non-catalytic reduction.

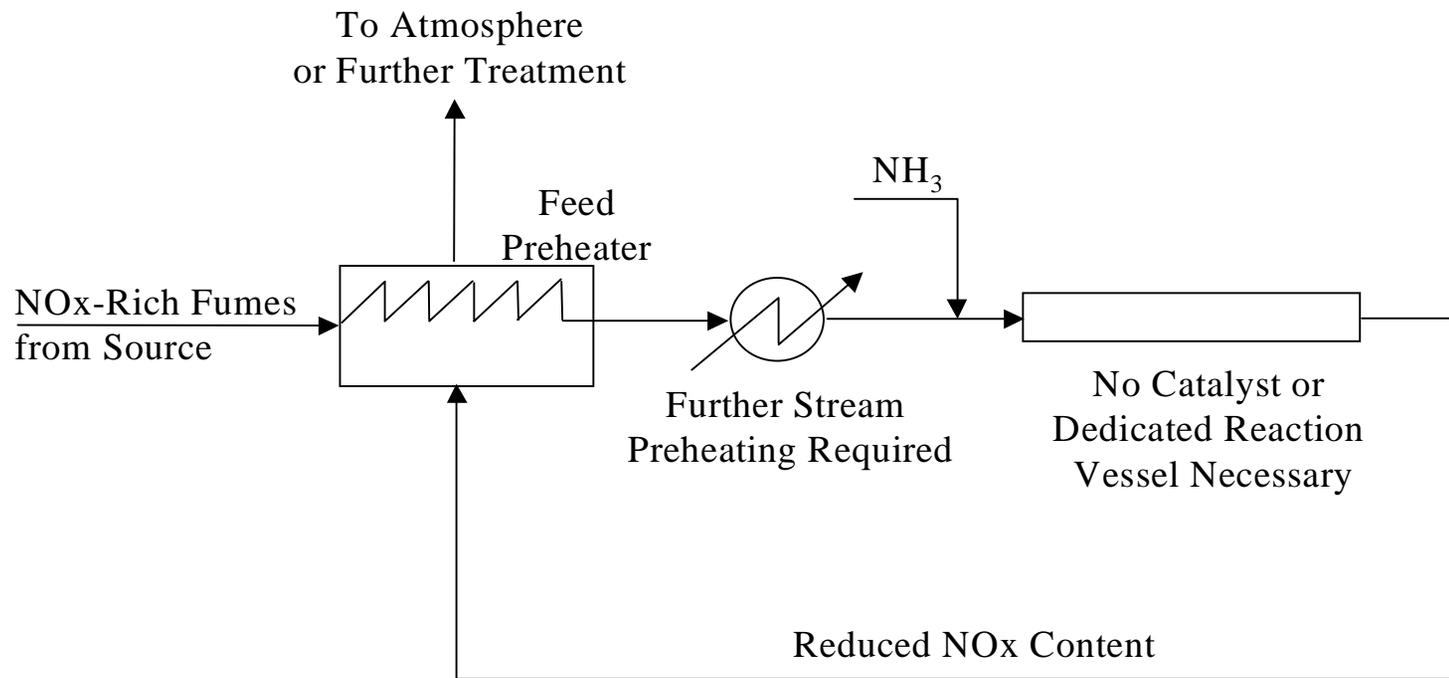


Figure 2.5. Flowsheet for a selective non-catalytic reduction (SNCR) process.

2.3 Catalyst Varieties for Selective Catalytic Reduction (SCR)

2.3.1 Catalyst Blends

A variety of catalyst blends are available for selective catalytic reduction. The important factors in selection of a catalyst blend include blend recipe, product selectivity, activation energy, pre-exponential factors, order of reaction with respect to the reactants, fouling and cleaning, competitive adsorption of inerts in the gas stream, catalyst cost, structural integrity, effective temperature range, and cost of reducing agent. Selectivity refers to the tendency of the catalyst to promote the reaction to the desired products. Undesired products would include NO_x production, as well as other species such as N₂O.

Most catalysts work by providing surface-active sites to which one or more of the reactants physically or chemically adsorbs. Adsorption to an active site stabilizes the molecule in a high-energy state of molecular orientation and bond angles that closely resemble the transition state for the reaction. The orientation of the molecule lowers the activation energy of the desired reaction and makes reaction more likely in the event of collision with other reaction molecules. A full surface chemistry and kinetic characterization study is beyond the scope of this work, but some aspects of the catalyst mechanism are key to understanding the effects they have on the reaction rate. Table 2.4 shows many of the catalysts available that promote the SCR reaction.

Table 2.4. Catalyst varieties used in SCR.

Platinum
Chromia on Titania ($\text{Cr}_2\text{O}_3/\text{TiO}_2$)
Manganese Oxide on Alumina ($\text{MnO}_x/\text{Al}_2\text{O}_3$)
Copper Oxide on Silica (CuO/SiO_2)
Copper Oxide on Bauxite ($\text{CuO}/\text{bauxite}$)
Copper Oxide on Alumina ($\text{CuO}/\text{Al}_2\text{O}_3$)
Vanadium on Titania ($\text{V}_2\text{O}_5/\text{TiO}_2$)
Vanadium on Alumina ($\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$)
Zeolites

Note: Bauxite is a support material blend of Al_2O_3 , SiO_2 , TiO_2 , and Fe_2O .

2.3.2 Catalyst Configurations

Vanadium on titania ($\text{V}_2\text{O}_5/\text{TiO}_2$) currently represents the most popular catalyst choice for SCR applications. We know that the weight percentages of the two main components of this catalyst blend strongly affect the catalyst characteristics. Research has shown that the configuration as well as the type and proportion of supporting material affect the activity and efficiency of the reactions promoted by vanadia catalysts (Marangozis, 1992). Also, these factors influence the orders of reaction with respect to the various reactants. Most researchers have found that the reaction order is zero with respect to ammonia (Marangozis, 1992). We can explain this observation by the fact that ammonia must chemisorb to the surface of the catalyst before reaction can occur. This chemisorption of ammonia occurs quickly, however, with the rate-limiting steps being the reaction of NO with bound ammonia and the chemisorption of O_2 on the surface. Figure 2.6 shows one mechanism proposed for ammonia binding to the surface of vanadia catalysts. Figure 2.7 shows one mechanism proposed for SCR on vanadia catalysts.

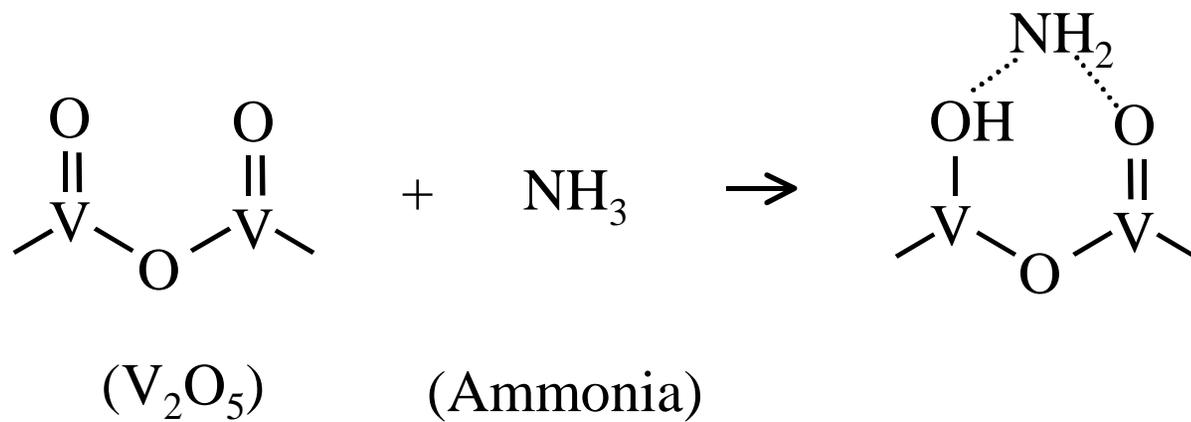


Figure 2.6. Proposed mechanism for ammonia binding to vanadia catalyst surface (Efstathiou and Fliatoura, 1995).

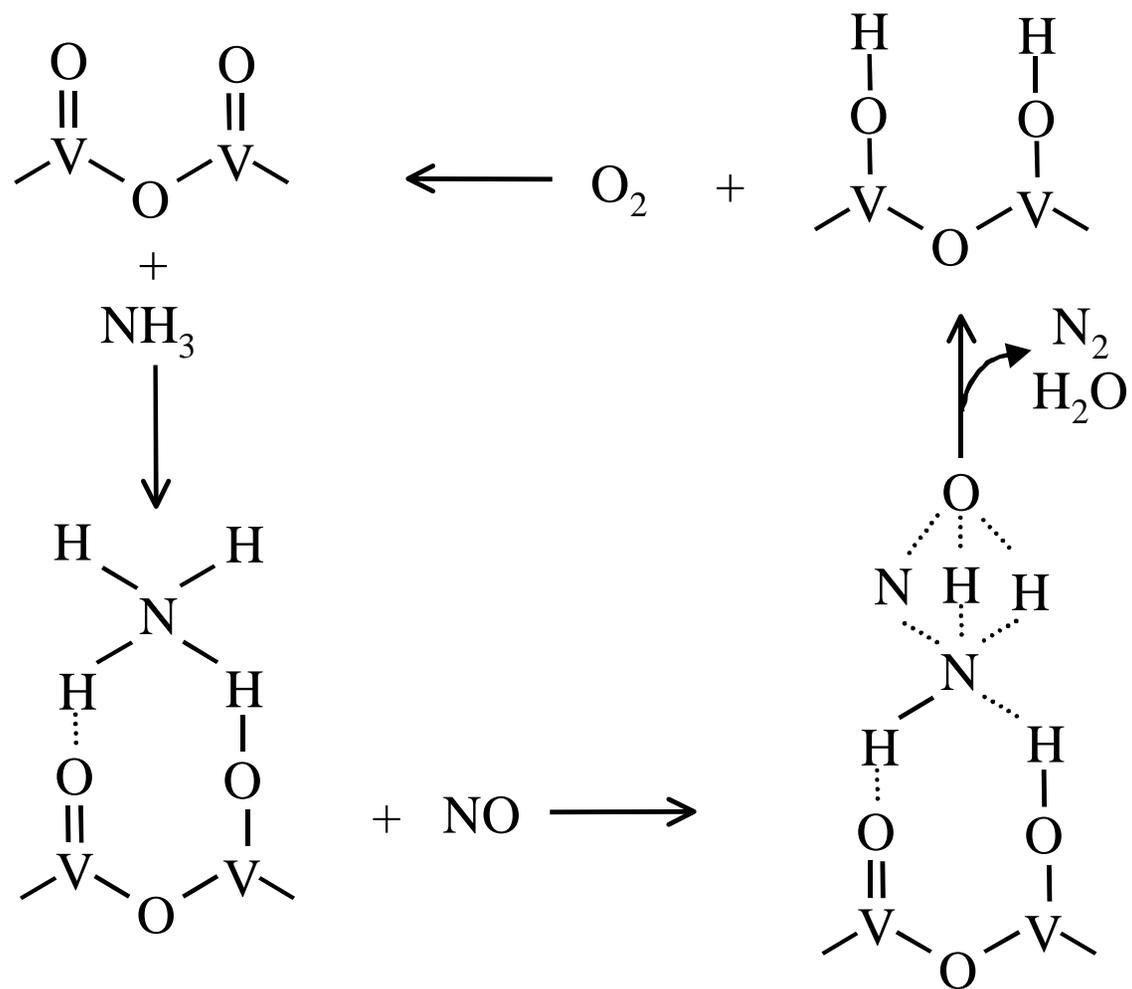


Figure 2.7. Proposed mechanism for SCR on vanadia catalyst surfaces (Marangozis, 1992).

2.3.3 Effect of Water on the SCR Reactions

Research has shown that water hinders the reaction rate for vanadia catalysts (Willi et al., 1996). Some evidence shows that the mechanism for water inhibition of the SCR reaction occurs because water prevents or slows the regeneration of the active catalyst sites for binding ammonia. The rate of reaction has been found to vary linearly with the number of V=O surface sites (Willi et al., 1996). One theory states that the presence of water slows the rate that V-OH sites react to become V=O sites (Willi et al., 1996). Figure 2.8 briefly illustrates the proposed mechanism for this theory.

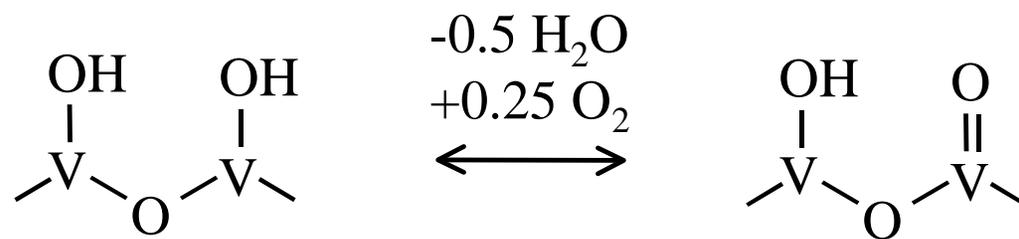


Figure 2.8. Importance of oxygen and the role of water inhibition to the reactivity of the vanadia catalyst surface.

2.4 NO_x Gas Absorption into Aqueous Media in Conjunction with SCR

For the design and optimization of a process linking NO_x absorption with SCR, the process engineer runs into all the typical issues for optimization of scrubbing, absorption, and reactors. He/she can make use of all the properties involved in these processes to his/her advantage. In addition, there are some peculiarities involved in the NO_x system that provide other opportunities for improving efficiency, but may also render conventional improvement techniques inconsequential.

A review and comparison of the relative usefulness of all correlations and empirical techniques that purport to be applicable to the processes involved in NO_x removal is beyond the scope of this work. Suffice it to say that attempts to apply conventional scrubber/absorber and reactor heuristics to this unique system give disappointing results in some situations. We discuss these particular situations in later chapters. Most of these cases manifest themselves in diminishing marginal returns (e.g., adding oxidizers in the liquor), whereas other widely accepted concepts may actually hinder the absorption performance (e.g., adding base to the liquor to neutralize acids). Below, we discuss typical engineering heuristics for the processes involved and how they relate to the unique properties of the NO_x.

For our case study, we use the NO_x abatement system in the tail gases of the nitrocellulose line at the Radford Facility and Army Ammunition Plant (RFAAP). RFAAP produces strong nitric acid in an ammonia-oxidation process. Among other applications, they use strong nitric acid to nitrate cotton linters for the production of nitrocellulose. The tail gases from the nitrocellulose line contain fairly high concentrations of NO and NO₂. A NO_x abatement plant treats these tail gases in an absorption column followed by a selective catalytic reduction vessel.

2.4.1 Equipment

2.4.1.1 Scrubber/Absorber

The NO_x absorption system at RFAAP consists of a single column, which houses a scrubber section in the bottom and a tray-absorber section in the top.

2.4.1.1a Scrubber

Scrubbers for contaminant removal come in a myriad of designs. The variety used at the RFAAP utilizes a two-stage spray design. The vapor feed located at the bottom stage blows the fumes through a mist generated by liquid spray nozzles at the top of each of the two stages. Liquid droplet size from the spray nozzles determines the interfacial area for mass transfer between the vapor and liquid phases.

2.4.1.1b Absorber

The absorber section of the column consists of 16 bubble-cap trays without an external cooling jacket. Filtered water feeds to the top of the column as the absorption liquor. Water collects on the trays to a depth that is controlled by the weir height. Vapor blowing through the submerged bubble caps provides interfacial contact and liquid mixing. Keeping the liquid and gas velocities within the optimum range contributes to bubble-cap tray efficiency. Although not included in the absorber installed at RFAAP, refrigerant trays are available that keep the absorber stages at a desired temperature.

2.4.1.2 Demister

The vapor flowing out of the top of the absorber entrains some liquid. This stream flows into the demister for removal of any liquid. The demister consists of a tank with wire-mesh

screens. Liquid impacts on the screens and flows out of the bottom of the demister to the waste drain, while vapor continues out the top of the demister unimpeded.

2.4.1.3 Process Heating Equipment

Combustion processes usually do not require additional stream heating equipment because the combustion temperature is adequate for the selective catalytic reduction reactions. Plants that do not produce NO_x gases at elevated temperatures still require units to affect the proper temperature change on the NO_x-rich streams. Waste gases at RFAAP arrive at the NO_x abatement only slightly above ambient temperature and require heating. The reduction reaction takes place at approximately 600 °F. Vapor leaves the absorber at 80 °F. A steam preheater heats the vapor stream to 100 °F. A heat exchanger known as an economizer uses the post-reaction gases to heat the pre-reaction gases from 100 °F to approximately 350 °F. A direct-fired heater uses natural gas combustion to complete the heating requirement, increasing the temperature from 350 °F to the reacting temperature of 600 °F (see Figure 2.4).

2.4.1.4 Catalyst Vessel

The catalyst vessel contains catalyst bundles in a honeycomb structure. NO_x gases are mixed with the appropriate reducing agent (ammonia in the case of SCR at RFAAP) and then fed into the catalyst vessel.

2.4.1.5 Stack

Gas flows from the catalyst vessel to the stack and out to atmosphere.

2.4.1.6 NO_x Analyzers and Process Control Equipment

A NO_x analyzer installed between the demister and the steam preheater tests NO_x concentrations leaving the absorber. Another, located in the stack, tests the gases leaving the

system. A control loop connected to the stack-gas analyzer controls ammonia feed to the catalyst vessel.

2.4.2 Species Involved

NO and NO₂ not only pose hazards to the external environment, they also are toxic to humans. In addition, NO₂ is highly corrosive and a strong oxidizing agent. Therefore, care must be taken to install proper piping and ducting that comes in contact with any NO₂-rich streams.

Ambient conditions do not favor the production of NO_x gases. Therefore, any appreciable quantities in the atmosphere must originate from man-made sources. These include processes carried out at extreme conditions of acidity, temperatures, and oxidizing conditions. The nascent species (NO and NO₂) are themselves harmful to humans and the environment; however, they are relatively short-lived and pose the most danger in the form they take after reacting in the environment. The transformations they make are slow but steady. The compounds do their damage and degrade to their more thermodynamically favorable and inert manifestations.

At atmospheric conditions, we find mixtures of NO and NO₂ in chemical equilibrium with N₂O₃ and N₂O₄. The absorption process to remove NO_x gases takes advantage of the solubility and subsequent reactivity in water of NO and NO₂ and their dimer forms (N₂O₃ and N₂O₄). Pure NO₂, N₂O₃ and N₂O₄, all liquids at ambient temperature and pressure, readily vaporize in less than saturating conditions due to their high vapor pressures. Therefore, temperature and pressure obviously play key roles in the absorption of these species into water. Low temperatures and high pressures tend to force the species into the liquid phase and facilitate both absorption and the ensuing exothermic reactions that take place in the liquid. These NO_x gases (NO, NO₂, N₂O₃, and N₂O₄) react with water vapor and in liquid water to form nitrous and nitric acids (HNO₂ and HNO₃, respectively). This fact illustrates quite clearly the acid rain threat posed by fugitive NO_x emissions.

Nitrous acid is very unstable and usually continues through the reaction mechanism to the more thermodynamically favorable nitric acid. Nitric acid is extremely stable in aqueous solution and represents the thermodynamic minimum for these compounds (at atmospheric conditions and the time-scale involved in most absorption processes).

Nitrous and nitric acid are capable of monoprotic-acid dissociation in aqueous solution. Nitric acid is a very strong acid and dissociates nearly completely. The fact that most of the nitric acid in solution exists as an ion, and that ions cannot vaporize, explains its high degree of stability in aqueous solution. In fact, it is this stability that determines the high absorption capacity of NO_x in water. Therefore, converting the NO_x gases to nitric acid constitutes the main objective of the NO_x absorption process.

2.4.3 Reactions in the System

Design engineers must inspect tabulated values and empirical correlations in the literature carefully before using these resources for design or retrofit of equipment. As stated above, the majority of the literature describes systems containing only NO. These data may or may not provide useful information to extend to NO and NO₂ systems. Also, whenever systems containing both NO and NO₂ are discussed, the NO_x concentrations usually referred to are blanket values incorporating NO, NO₂, N₂O₃, and N₂O₄. All these compounds are present at equilibrium in NO_x systems involving NO and NO₂, and each has subtly different properties.

Researchers may correlate absorption rates based on concentration data for NO and NO₂. Because it is difficult to isolate these compounds from the contributions of N₂O₃ and N₂O₄, these rates represent a murky conglomeration for absorption rates of all the compounds in the system. This fact makes the synthesis of an accurate model that incorporates literature data somewhat of a paradox. The spectrum of chemistry that takes place after the absorption of these species into aqueous solution complicates issues further. Inspection of the system shows clearly that absorption equilibrium estimates for the individual species, usually used for absorber column design, have little pertinence to the application of such a process to the NO_x and water system.

The real driving force for NO_x removal and the properties that must be used to the best advantage are those of the myriad of reactions and solubilities for the different species. It is only a fortunate coincidence that most conventional design heuristics applied to this system do less harm than good.

Cheremisinoff and Young attempt to list all the reactions for NO_x in water on page 671 in part two of their book, *Air Pollution and Control and Design Handbook* (Cheremisinoff and Young, 1977). The pertinent reactions appear in Table 2.5 as follows:

Table 2.5. Reactions involving NO_x in air and water
(Cheremisinoff and Young, 1977).

2.1	$2\text{NO} + \text{O}_2 \leftrightarrow 2\text{NO}_2$
2.2	$2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$
2.3	$3\text{NO}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{HNO}_3 + \text{NO}$
2.4	$\text{N}_2\text{O}_4 + \text{H}_2\text{O} \leftrightarrow \text{HNO}_3 + \text{HNO}_2$
2.5	$2\text{HNO}_2 \leftrightarrow \text{NO} + 1/2\text{N}_2\text{O}_4 + \text{H}_2\text{O}$
2.6	$3\text{HNO}_2 \leftrightarrow 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$
2.7	$\text{NO} + 3/4\text{O}_2 + 1/2\text{H}_2\text{O} \leftrightarrow \text{HNO}_3$

The reader can see that these equations are extensive, except they do not include N₂O₃ nor any description as to the phase in which the reactions predominate. These reactions represent a good start towards a keener understanding of the system. A preferred source would delineate the reactions into the vapor or aqueous phase. Better still would be the incorporation of solubility data and relative reaction rate and equilibrium information, so the engineer can whittle down the complex system above into a manageable model that is both more accurate than conventional heuristics, as well as simplified enough to be useful.

We require an assessment of the important species and reactants. From this assessment and further assumptions, we can perform systematic elimination of negligible or redundant pathways to bring the absorption mechanism into a manageable form. For such a treatment, we

shift our attention from review books and comprehensive treatises on pollution control to research papers, focusing more closely on the NO_x and water system.

D. N. Miller, in his paper, “Mass Transfer in Nitric Acid Absorption,” describes the NO_x and water system in great detail (Miller, 1987). According to Miller, the reaction system can be divided into three paths. These paths are distinct, but they are not independent. Further, Miller categorizes the reactions into the phase in which they predominate. Table 2.6 shows the mechanism for NO_x absorption as described by Miller.

Table 2.6. Full reaction and absorption mechanism for NO_x and water (Miller, 1987).

N ₂ O ₄ Path	N ₂ O ₃ Path	NO ₂ Path
Gas Phase	Gas Phase	Gas Phase
$2\text{NO} + \text{O}_2 \leftrightarrow 2\text{NO}_2 \quad (2.8)$ $2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4 \quad (2.9)$	$\text{NO} + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_3 \quad (2.13)$	$\text{NO}_{2(\text{g})} \leftrightarrow \text{NO}_{2(\text{l})} \quad (2.17)$ $2\text{NO}_{2(\text{l})} + \text{H}_2\text{O} \leftrightarrow \text{HNO}_3 + \text{HNO}_2 \quad (2.18)$
Transport	Transport	Transport
$\text{N}_2\text{O}_{4(\text{g})} \leftrightarrow \text{N}_2\text{O}_{4(\text{l})} \quad (2.10)$	$\text{N}_2\text{O}_{3(\text{g})} \leftrightarrow \text{N}_2\text{O}_{3(\text{l})} \quad (2.14)$	$\text{HNO}_{3(\text{g})} \leftrightarrow \text{HNO}_{3(\text{l})} \quad (2.19)$
Liquid Phase	Liquid Phase	Liquid Phase
$\text{N}_2\text{O}_{4(\text{l})} + \text{H}_2\text{O} \leftrightarrow \text{HNO}_3 + \text{HNO}_2 \quad (2.11)$ $3\text{HNO}_2 \leftrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}_{(\text{g})} \quad (2.12)$	$\text{N}_2\text{O}_{3(\text{g})} + \text{H}_2\text{O} \leftrightarrow 2\text{HNO}_2 \quad (2.15)$ $2\text{HNO}_2 + \text{O}_2 \leftrightarrow 2\text{HNO}_3 \quad (2.16)$	$3\text{NO}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{HNO}_3 + \text{NO} \quad (2.20)$

Note: (l) refers to liquid phase, (g) refers to gas phase

Miller concludes that the oxidation of NO, reaction (2.8), induces a major rate limitation in this sequence when the initial NO_x gas is composed primarily of NO. In this case, the oxidation of NO to NO₂ proceeds so slowly that the remainder of the reactions can only continue as fast as the oxidation reaction. However, as we state previously, the NO_x gases in nitric acid plant off-gases already contain mixtures of NO and NO₂. Therefore, NO_x gases from typical nitric acid plants bypass this rate limitation. Miller also states that the reverse reaction of reaction (2.8) can be neglected.

The NO₂ route of absorption is slow relative to the routes for N₂O₃ and N₂O₄ and can usually be neglected in rate studies. He assumes that the primary chemical steps in the N₂O₄ path are rapid and achieve equilibrium. However, the N₂O₄ absorption step, reaction (2.10), represents another rate-limiting factor.

Once in the liquid film near the phase interface, consumption of N₂O₄ by reaction (2.11) rapidly goes to completion. Miller draws an interesting conclusion here. He suggests that there should be a negligible concentration of N₂O₄ in the liquid, even though there is an appreciable amount of NO₂. Therefore, the reaction of dimerized NO₂, i.e., N₂O₄, with a water molecule to form nitric acid in the liquid, reaction (2.11), is much faster than reaction (2.20) that involves two NO₂ molecules colliding with a water molecule. Stated in this way, the conclusion is rather intuitive due to the low probability of two NO₂ molecules colliding in the liquid phase.

The overall stoichiometry for reactions (2.11) and (2.18) are the same, however, the rate difference is modulated by the frequency of collision NO₂ molecules in aqueous solution. If reaction (2.18) is elementary, then the reaction must happen as it is written, and two NO₂ molecules must simultaneously collide and react with a water molecule. Obviously, water molecules are in large excess in aqueous solution. NO₂ molecules are quite rare, however, due to its low solubility. Therefore, the probability of two NO₂ molecules colliding is quite low. More likely, colliding NO₂ molecules dimerize to form N₂O₄. Then N₂O₄ quickly reacts with water to form nitrous and nitric acid.

N_2O_3 represents the product of the coupling reaction between NO and NO_2 molecules, reaction (2.13). N_2O_3 can also dissolve into the liquid, although according to Miller, “absorption of N_2O_3 is small compared to that of N_2O_4 and can be omitted without appreciable error in most column simulations.”

This explanation allows us to combine the NO_2 and N_2O_4 paths and neglect the N_2O_3 path. These, combined with other assumptions, say that the concentration of N_2O_4 in the liquid controls the rate of production of nitric and nitrous acid in the aqueous solution. N_2O_4 arrives in the liquid through direct absorption from the vapor and by dimerization of NO_2 molecules which have themselves been absorbed (N_2O_4 in water goes to the acid products quickly and does not decompose to NO_2). Nitrous acid is unstable, and Miller states that its transient existence is often eliminated from the mechanism by combining reactions (2.11) and (2.12). The result of this combination appears below. We label this reaction (2.11,12).



Reaction (2.16) shows that oxidation of HNO_2 by soluble O_2 is an alternate pathway for nitric acid production, although Miller neglects this contribution (presumably on the basis of the lack of literature values for this oxidation rate). The low solubility of O_2 tends to drop this pathway. By neglecting the N_2O_3 pathway, HNO_2 can decompose in two ways. It can combine with nitric acid in the reverse of reaction (2.11), or via the forward reaction (2.12). Since reaction (2.12) takes place in the liquid and generates NO which predominates as a vapor, the reverse of reaction (2.12) can most likely be neglected. Nitric acid is a monoprotic strong acid and dissociates quickly and nearly completely. Therefore, it is highly stable in the aqueous solution.

The reverse of the process described above does not negatively affect NO_x absorption performance. Therefore, efforts to completely neutralize the acid by the addition of base are superfluous. The rates of the forward and reverse reactions, the equilibrium of reaction (2.11), and the forward rate of reaction (2.12) appear to be most important in the determination of the overall rates of NO_x absorption and nitric acid production. The scrubber/absorber performance follows from the determination of these overall rates. Cheremisinoff and Young (1977) contend

that the maximum amount of total NO_x that can be removed is 66.66 percent (2/3). They arrive at this by assuming the overall absorption reaction is given by the following:



Thus, for every three moles of NO₂ consumed, one mole of insoluble NO is evolved. As stated previously, the oxidation rate of NO to NO₂ is slower than the typical time scale for NO_x absorption operated at atmospheric pressure. To be sure, reaction (2.20) represents a drastic simplification of the system and contains little value as to the kinetic nature of the mechanisms. However, the proposal of a maximum efficiency of the NO_x absorption process gives a useful optimum for the engineer to attempt to achieve. Attempts to reach or exceed this ‘maximum’ may prove disappointing and expensive as diminishing returns take hold. Once the NO₂ content is diminished, it is time to send the stream to the SCR to deal with the NO.

2.4.4 Flue-Gas Treatment Versus Nitric Acid Production

The majority of the research done on the absorption of NO_x gases in water and nitric acid solutions approaches the problem from the perspective of nitric acid production. However, the operating conditions for NO_x absorption for typical flue-gas treatment processes differ considerably from those of typical nitric acid production units. Due to the complexity of the system as outlined in the previous section, the difference in operation conditions requires different strategies for optimization.

2.4.5 Current Research

Thomas and Vanderschuren (1997) describe an interesting aspect of the NO_x and water system in their paper “The Absorption-Oxidation of NO_x with Hydrogen Peroxide for the Treatment of Tail Gases.” They observe a dramatic increase in NO_x absorption performance with increasing acid concentration in the scrubbing liquid containing H₂O₂. They attribute this effect to the catalytic action of free protons on the oxidation reaction of HNO₂.

They contend that H_2O_2 , added in slight stoichiometric excess relative to NO_x species, rapidly oxidizes HNO_2 to HNO_3 so that no HNO_2 can react with HNO_3 to produce NO_2 . In the absence of H_2O_2 , nitric acid concentration reduces absorption performance. Just as mentioned previously, HNO_2 reacts with excess HNO_3 to yield NO_2 (the reverse of reaction (2.18)). NO_2 can quickly desorb into the gas phase, reducing absorption efficiency. Figure 2.9 shows the positive effect of HNO_3 concentration on NO_x absorption in the presence of H_2O_2 .

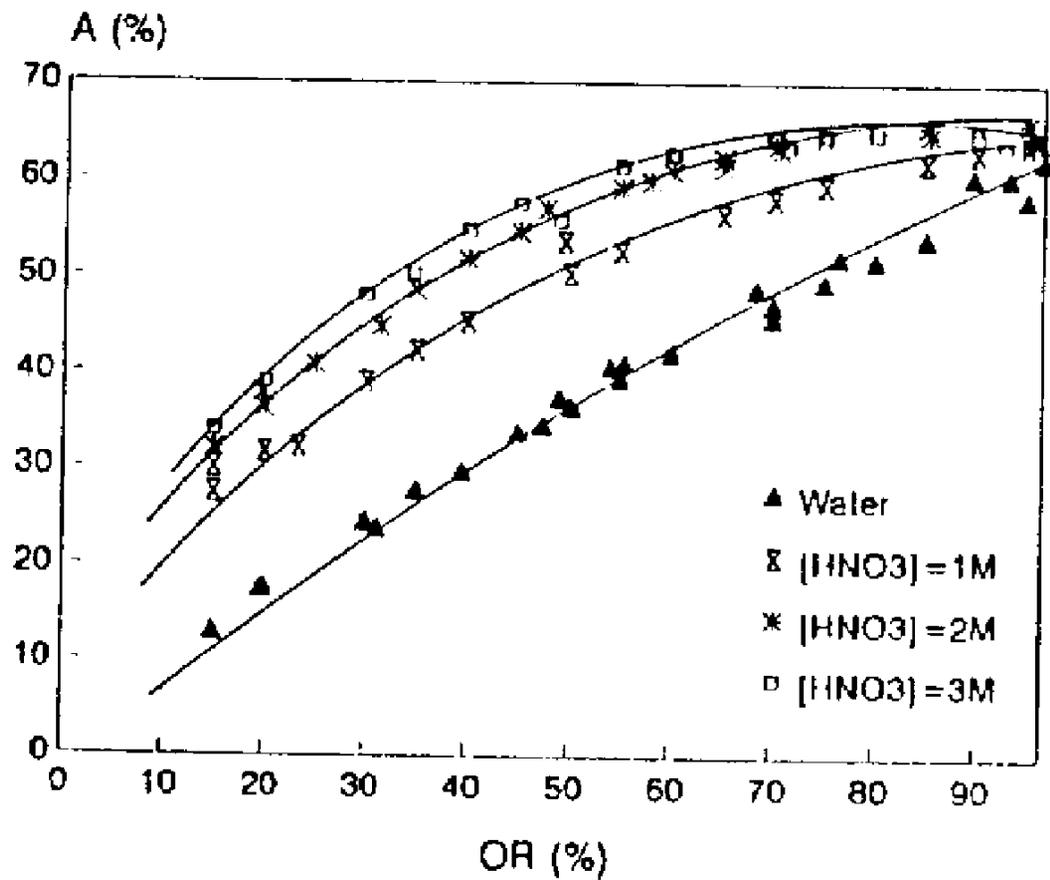


Figure 2.9. The effect of nitric acid on NO_x absorption in hydrogen peroxide solutions (Thomas and Vanderschuren, 1996). A (%) is the percent of absorption of NO_x, OR (%) is the percentage of NO_x that is in the NO₂ and N₂O₄ form, the remainder being in the NO form.

In the absence of H_2O_2 , the catalytic activity of hydrogen ion (H^+) probably competes with the reverse reaction that regenerates NO_x gases. H_2O_2 eliminates the reverse pathway of reaction (2.18), therefore eliminating the negative effect of acid concentration on NO_x absorption. In this instance, dissociated nitric acid actually increases the overall rate of NO_x absorption. However, acid concentration only begins to affect absorption performance dramatically at molarities above 5 mol/L. Like nearly all catalysts, H^+ ions most likely do not favor either the forward or reverse reaction, they just serve to bring the reactions to equilibrium more quickly.

The important reactions take place in the liquid film, and at low acid concentration, equilibrium is favorable for NO_x absorption. At high nitric acid concentrations, equilibrium becomes increasingly antagonistic to our NO_x abatement objectives, and the driving force of absorption that determines the rate decreases. Engineers hoping to remove NO_x gases typically do not appreciate the tendency for H^+ ions to hasten the system to an unfavorable equilibrium.

Direct oxidation of HNO_2 by H_2O_2 eliminates reaction (2.12) as well. This HNO_2 dissociation reaction, $3\text{HNO}_2 \leftrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}_{(\text{g})}$, evolves insoluble NO . This reaction gives 1 mole of NO for every 3 moles of NO_2 absorbed and converted to HNO_2 . This production of a molar ratio of 1 to 3 of NO to NO_2 absorbed gives rise to the 2/3 NO_x absorption maximum, essentially another source of reduced absorption efficiency. In the absence of H_2O_2 , direct HNO_2 oxidation can only occur in the liquid by combination with O_2 , via reaction (2.16), $2\text{HNO}_2 + \text{O}_2 \leftrightarrow 2\text{HNO}_3$.

The low solubility of O_2 in water, low concentrations of the unstable HNO_2 , the lack of documented kinetic values in the literature, and support for the existence of the 66% maximum NO_x removal barrier (Cheremisinoff and Young, 1977) all suggest that reaction (2.16), $2\text{HNO}_2 + \text{O}_2 \leftrightarrow 2\text{HNO}_3$, is not a major pathway in the absence of a strong oxidizer. However, if H_2O_2 promotes the oxidation of HNO_2 over reaction (2.12), $3\text{HNO}_2 \leftrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}_{(\text{g})}$, then it is fairly obvious that the overall absorption performance will improve. In fact, if direct oxidation of HNO_2 can be promoted exclusively by H_2O_2 , then the 2/3 NO_x absorption limit can be

breached. The use of H_2O_2 provides advantages over other oxidizing agents in its relative safety and lack of pollutant by-products.

2.4.6 Modifications and Retrofit Options for Existing NO_x Absorption Plants

One of the most obvious improvements that can be made at existing nitric acid plants is the improvement of the NO_x gas-absorber performance. However, typical design and optimization heuristics for scrubber/absorber systems may not have satisfactory effects on the unique NO_x absorption case studied here.

There are some simple studies that can be done to make sure that the tower is operating properly. In the book *Wet Scrubbers*, Second Edition, by Kenneth C. Schiffner and Howard E. Hesketh (Schiffner and Hesketh, 1996), the authors give a fairly extensive checklist of items to consider when designing or optimizing gas absorption systems. Most of checklist points do not apply to the issue at hand, concerning themselves with packed towers and particulate removal. We are interested in gas absorption in a tray tower. Some of the points are apt. Point (11) suggests end weirs for a uniform head of water on the tray, eliminating a gradient of water coverage. Points (15), (16), and (17) suggest adhering to the gas and liquid flow ratings for the tower. Increasing the flow of either gas or liquid will reduce the overall efficiency of the scrubber and may not even impact the overall absorption (i.e., more water fed may not translate into more contaminant removed).

In the *Air Pollution Control and Design Handbook* (Cheremisinoff and Young, 1977), the authors make three points about high-efficiency NO_x removal. First, scrubbers must have a high retention time to allow for the slow oxidation rate of NO to NO₂. Secondly, the half-life of NO concentration increases with decreasing influent concentration as shown in Figure 2.10. Therefore, it is very difficult to reduce low influent concentrations beyond a certain extent. The engineer should strive to minimize NO_x stream dilution prior to treatment. The figure shows that the oxidation rate of NO to NO₂ (Reaction (2.8) $2\text{NO} + \text{O}_2 \leftrightarrow 2\text{NO}_2$) can be neglected for small concentrations of NO. However, the reaction becomes increasingly important with higher NO concentration.

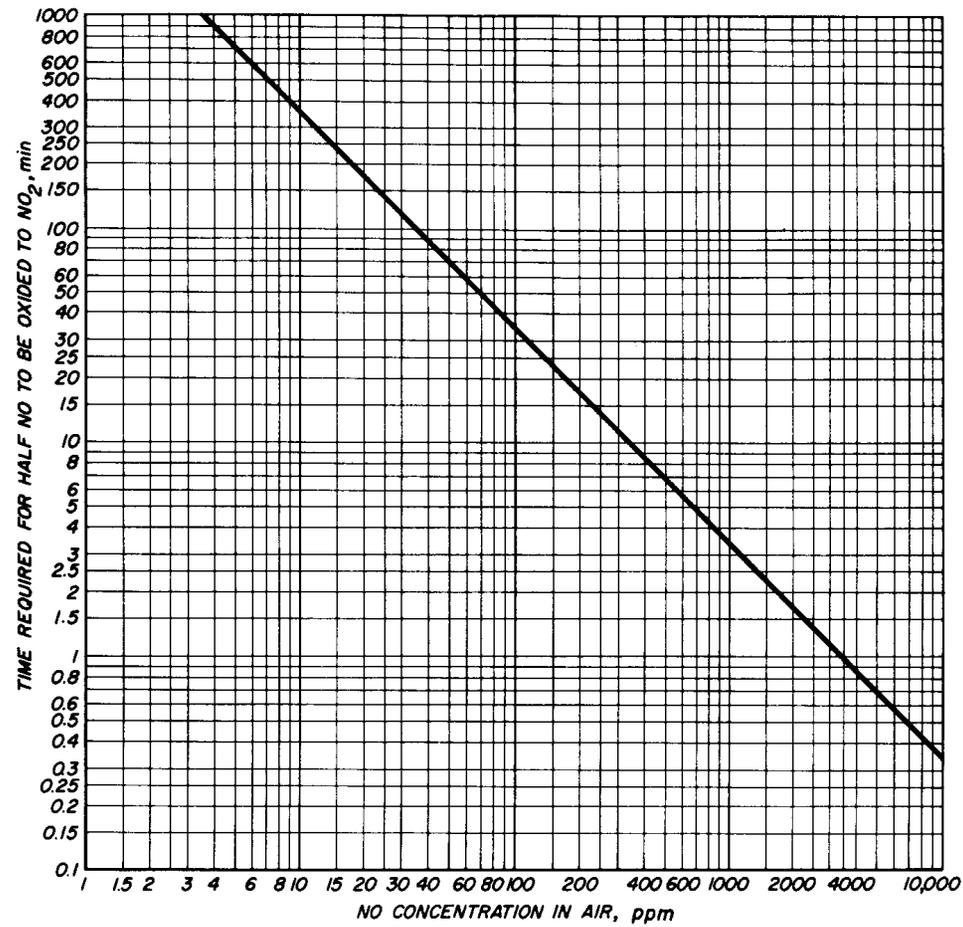


Figure 2.10. Plot of the time required for half of the initial NO to be oxidized to NO₂ at ambient conditions. The abscissa represents the initial NO concentration, and the ordinate gives the corresponding half-life time for that initial NO concentration (Cheremisinoff and Young, 1977).

Thirdly, because NO is insoluble for all practical purposes, and one mole of NO is evolved for every three moles of NO₂ converted to HNO₃, absorption can theoretically attain a maximum of 66.67% (2/3) NO_x removal. This maximum can be achieved, assuming that nearly all the NO_x fed to the absorber is NO₂ and that absorber operation is ideal in all other aspects. Most absorbers fall well short of this ideal of operation. However, the concept of a maximum attainable NO_x removal gives the engineer a goal to strive for and an idea of what he/she can realistically expect from the equipment.

Cheremisinoff and Young also mention the use of alkaline solutions to neutralize the acids produced in NO_x absorption. They suggest that such an expedient gives only a slight improvement. The use of alkaline solutions proves disappointing in this case because, unlike most absorption operations, the back pressure of the absorbed species (NO₂ quickly reacts to HNO₃ in this case) is not the major resistance. In fact, the engineer's toughest opponent is the slow rates of mass transfer and the rates of the slow reactions in the system. Optimization approaches must therefore focus on optimizing reaction and mass-transport conditions for phase transfer of critical species.

2.4.6.1 Cooling

Temperature reduction improves absorption performance in several ways. First, low temperatures favor NO₂ over NO. Second, low temperatures favor N₂O₄ over NO₂. Thirdly, the vapor pressures of N₂O₄ and NO₂ increase with increased temperatures. Fourthly, nitric acid production and dissociation are exothermic reactions, favored at lower temperatures. Figure 2.11 illustrates the findings of Cheremisinoff and Young (1997) for the response of NO_x absorption to changes in temperature.

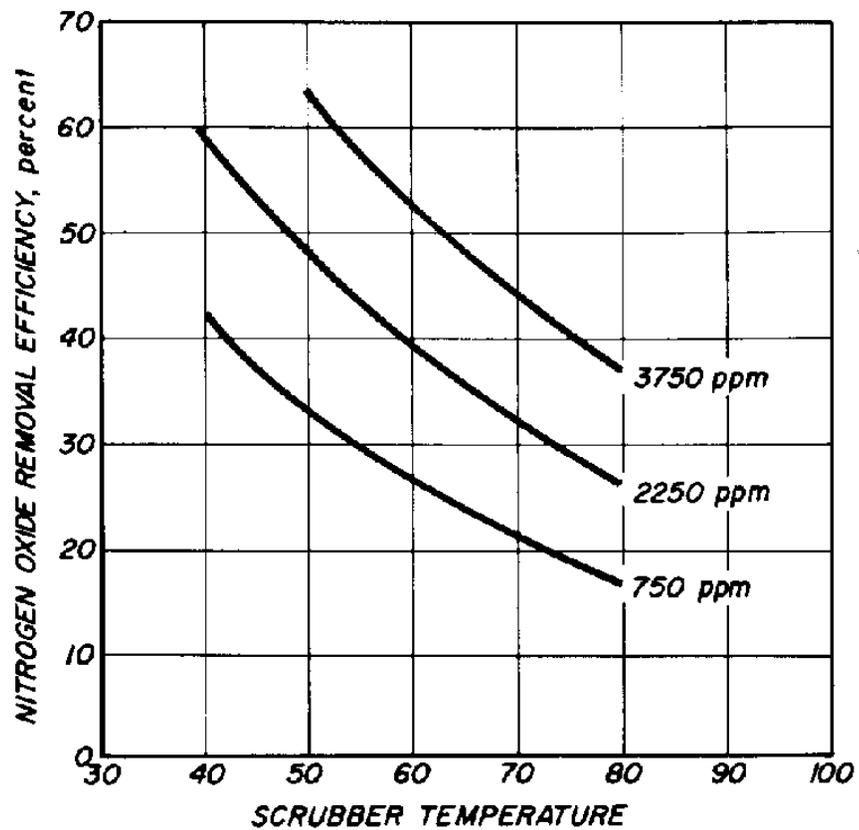


Figure 2.11. Plot of NO₂ removal efficiency versus scrubber temperature for three different initial concentrations of NO₂ (Cheremisinoff and Young, 1977).

Various methods of cooling the system are available. Refrigerant trays that can control the temperature of each stage represent the ideal solution. A cooling jacket on the column and chilling the water feed are alternative methods. Interstage chillers can be incorporated to control liquid temperatures. Costs to cool the fume feed may prove prohibitive due to the usual presence of high volumes of air, with notoriously poor heat-transfer properties, requiring large heat-exchanger contact areas.

2.4.6.2 High-Pressure Operation

Increasing absorber pressure has a positive effect on the gaseous reactions and the vapor pressures of the soluble species. The equilibrium of both the reactions, $\text{NO} + \text{O}_2 \leftrightarrow \text{NO}_2$ and $\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$, is driven to the right considerably by raising the pressure. Increased pressure also indirectly helps the liquid-phase reactions. Because NO_2 and N_2O_4 are liquids with very high vapor pressures at ambient conditions, increased pressure considerably stabilizes their absorption into water. With higher concentrations of these compounds in the liquid, the rates and equilibria of their reactions to nitric improve.

2.4.6.3 Addition of H_2O_2

Adding hydrogen peroxide to the filtered water feed would improve absorption. An extra benefit of the addition of H_2O_2 is that increased nitric acid concentration actually helps the absorption of NO_x gases. The mechanism for this autocatalytic effect is not fully understood, nor is it known exactly why H_2O_2 is required to bring about this effect. H_2O_2 , though expensive, is a good candidate because the product of its reaction is simply H_2O . This product obviously does not add to the wastewater treatment duty of the plant.

2.4.6.4 Oxidation of Nitric Oxide

In an interesting mechanism elucidated in the book *Basic Nitrogen Compounds* (Matasa and Tonca, 1973), Matasa and Tonca show nitric acid to be a catalyst in the oxidation of nitric oxide. Table 2.7 shows this proposed catalysis mechanism in detail.

Table 2.7. Mechanism for nitric acid catalyzed NO oxidation

(Matasa and Tonca, 1973).



Contacting an NO-rich stream with concentrated nitric acid can speed its oxidation to NO₂. The NO₂ formed can be recycled to the absorber where it can be absorbed. Making minimal changes, the engineer can run the absorber at the optimum nitric acid concentration to maximize the catalytic effect, while keeping the equilibrium limitation of the NO₂ absorption at a reasonable level. Although the equilibrium becomes unfavorable to NO₂ absorption at high nitric acid concentrations, in general, equilibrium is not achieved and the rates of reaction are the biggest resistance to absorption. A countercurrent flow system contacting high NO and high nitric acid concentrations should be explored.

2.5 Computer-Modeling Techniques

2.5.1 Special Challenges of NO_x Absorption

The unit-operation method is currently the most widely used technique for designing and modeling equipment to be used in a chemical process. The unit-operation approach makes use of equilibrium data and empirically derived rate expressions to estimate the behavior of equipment under operating conditions. These techniques are usually acceptably accurate for unit operations driven by equilibrium forces and containing few chemical processes.

For systems that vary from equilibrium, the usual expedient is to assume a typical efficiency for that particular unit operation. Engineers functionally define the efficiency as the degree to which the actual process achieves the equilibrium condition. This concept, although quite useful in well-behaved systems, presents problems when dealing with a complex system that is far from equilibrium.

The design engineer must specify the efficiency for staged towers in one of three ways. An overall column efficiency represents the number of equilibrium stages divided by the number of actual stages required to complete the desired separation. A stage efficiency describes the transfer of a substance from one phase to the other divided by the amount transferred if vapor and liquid leaving the tray were allowed to achieve equilibrium. Point efficiency describes the degree to which equilibrium is reached at individual locations on the stage. The point efficiencies across the stage are integrated to give the overall stage efficiency.

The reader should have noticed a problem with these techniques, which becomes more important as we go from the first to the last technique. First, detailed equilibrium data must be available for the system. Second, the engineer must have detailed information on how the system he/she is working with is going to behave. In the case of the point efficiency, he/she must know how the system behaves at small intervals across the tray. Good equilibrium data are a luxury; a priori data on system behavior are mythical. Too many variables affect the way a system will behave under different circumstances.

The difficulties encountered when researchers and engineers attempt to characterize the NO_x absorption system expand on those encountered in even simple absorption processes. The NO_x system provides the engineer with all the difficulties mentioned above. It also adds several other factors that he/she must deal with when describing the system. Multiple reactions occur in the vapor and liquid phases. Variables such as temperature and pressure affect the rates of these reactions. However, the resistance to diffusion of reactants and products between the phases has a major effect on the progress of the reactions.

The high vapor pressures and low solubility of NO_x gases makes their absorption dependent upon the rate at which the reactions consume soluble NO_x species, thus creating room for more to absorb. Reactions control the diffusion, just as diffusion controls the reactions. To complicate matters, the product of the reactions (HNO₃) catalyzes some of the reactions. The system has intimately coupled diffusion and kinetic problems. Each is complicated indeed on its own merit. Design issues, such as different tray and packing types, as well as the large range of process variables demand to be reckoned with. The wealth of plots and empirical correlations of extremely limited value in the literature gives evidence of the inability to neatly package all the intricacies of NO_x absorption for the engineer in the field. We need a fundamental approach to a specific application.

The prevalence of personal computers makes exploration of complex differential equations possible. Chemical process modeling software allows the engineer to apply multiple design options, retrofits, and process variable modifications to the unit operation he/she wishes to explore. Both of these uses of computers are capable of generating huge quantities of “usable” data in a short amount of time. However, the engineer must take great care to ensure the usefulness and correctness of the information.

2.5.2 *ASPEN Plus*

The ASPEN Plus software package is one such chemical process-modeling tool. It uses thermodynamic calculations and individual unit-operation models, called blocks. These blocks can be linked together to model an entire process or plant. ASPEN uses numerous well-known direct and iterative calculation techniques when modeling the unit operation blocks. For example, an engineer can specify a Fenske-Underwood-Gilliland (FUG) model for the shortcut design of a distillation column. After specifying operating parameters for the column, such as column operation pressure, operating reflux ratio and number of stages, and the input feed specifications, ASPEN calculates the required number of equilibrium stages using the FUG approach. Rigorous methods that are more accurate but also require more calculations can be used as well.

ASPEN is primarily a rating or retrofit tool, however, designs can be explored by use of trial and error. For rigorous column models, the engineer must specify the total number of stages, feed-stage location, etc., for a column he/she wishes to model. From this, ASPEN calculates the output-stream conditions.

When designing a new process with ASPEN, the engineer must specify equipment design variables in an iterative process until the simulated process matches the design specifications desired. We are primarily concerned here with process retrofit and optimization. First, we develop an accurate and robust computer model in ASPEN Plus. Such a model is capable of simulating the available data representing the true operational performance of the system. After establishing this working model, we incorporate adjustments in the process parameters of the computer simulation. We observe the results of these process changes. For example, these process changes and the related results could include the positive effects of process optimization, or the negative effects to the system due to loss of process utilities (e.g., loss of cooling water flow to a reactor).

Next, we perform sensitivity analyses to determine the dependence of output variables on manipulated variables (e.g. the effect column pressure has on NO_x concentration leaving the top of the column). ASPEN Plus can generate plots and figures from the simulation data for a visual representation of these trends.

Finally, we can simulate various competing retrofit and process optimization options on the computer. The model helps us assess the relative effectiveness and economic viability of the options. We know that the model behaves as the real system does before retrofit. We have confidence that the model accurately simulates how the system will behave after the retrofit options and changes in process variables are implemented. In this way, we can judge all these options based on the simulated performance of the process.

The unit-operation modules available in ASPEN cannot accurately model certain real units that combine many chemical processes. As detailed earlier, the scrubber/absorber column performs the tasks of a scrubber, an absorber, and a reactor. Modeling this process accurately in

ASPEN with a single tower would be difficult (if not impossible). This is not generally a problem, because we can separate the different processes into individual ASPEN blocks and achieve accurate results. This procedure also gives the added benefit of independent inspection of each separate process individually, although separating the processes does create some problems.

The simulation engineer must configure the ASPEN model to accurately simulate the behavior of the real process. He/she can represent the scrubber/absorber (and reactor) as multiple blocks in ASPEN. For instance, he/she could use two scrubber tanks (two-phase flash drums) to represent the scrubber section. These calculate vapor-liquid equilibrium, but do not allow for the incorporation of reactions. At the top, the use of a reactive absorption column simulates the staged absorber. The engineer can also incorporate the reactions in stoichiometric, equilibrium, or kinetic reactor models. Model accuracy depends on a careful arrangement of these reactors, because the reactions in the real process most likely run the whole height of the tower.

2.5.3 Fundamental Approach

Fundamental studies of diffusion and reaction mechanisms generally do not directly apply to the design of equipment or process conditions. However, these studies can tell the engineer what factors are important and what factors can be ignored in the empirical correlations and heuristics most often used for unit operation design. As computing power increases in speed and availability, fundamental mathematical models will almost assuredly play a more important role in process design and simulation. They may never replace the empirical unit-operation approach but they will take their place alongside it. Properly used, mathematical models can determine parameters that the engineer can use in his/her unit-operation model. Previously, the engineer had to find empirical data describing a similar unit operation with similar operating conditions to identify accurate parameter values. Mathematical mechanistic models rely less on empirical studies and more on fundamental thermodynamics kinetic data for reactions and diffusion that are more easily generalized to related processes.

2.6 Summary

NO_x gases threaten both plant and animal life. They are poisonous in their incipient form and also contribute to the depletion of atmospheric ozone, as well as forming smog and acid rain via complex reactions in the atmosphere. Due to the short lifetime of NO_x gases in the environment, the harmful effects from them concentrate over urban and industrial areas with high output levels of the compounds. Thermodynamics does not favor the production of NO_x from N₂ and O₂ at atmospheric conditions, therefore the exploits of man represent the source for these harmful gases.

Man-made NO_x consists mostly of NO and NO₂. Most of the stationary sources of NO_x have NO as the main component of total NO_x with little NO₂ present. Nitric acid plants are special in that they contribute primarily NO₂ in their NO_x off-gases. However, the effluents from nitric acid plants contain appreciable amounts of NO as well. The presence of such a mixture makes treatment methods aimed at NO or NO₂ alone inappropriate and ineffective at total NO_x reduction.

A wide variety of technologies have been developed for reduction of NO_x in flue-gas emissions. We loosely categorize these into wet and dry processes. Here, we focus on the wet processes of wet scrubbing and extended absorption and the dry processes of non-selective catalytic reduction (NSCR), of selective catalytic reduction (SCR), of selective non-catalytic reduction (SNCR).

Wet scrubbing, also known as the sodium acetate process, eliminates NO via a chain reaction in a scrubbing liquid. SO₂ and sodium acetate expedite the absorption of NO which eventually converts to N₂ in a complex network of aqueous reactions. Removal of the solid and liquid waste derived from the aqueous reactions represents a major drawback of wet scrubbing. Also, although wet scrubbing simultaneously eliminates SO₂, it depends on the proper stoichiometric ratio of SO₂ to NO for efficient operation.

Extended absorption consists simply of the installation of additional absorption towers to an existing absorption system. This process finds the most usefulness for nitric acid plants where the absorbed NO_x contributes to the product stream.

We differentiate the family of reductive dry processes for NO_x removal by their reducing agent and whether or not they utilize a catalyst. Different operation temperatures further distinguish between the three processes.

NSCR utilizes the components of natural gas, CH₄, CO, and H₂, to chemically reduce NO_x to N₂ and H₂O over a catalyst bed. The use of natural gas requires a temperature of approximately 900 °F (482 °C) whereas the use of H₂ requires a temperature of 300 °F (149 °C). NSCR can give approximately a 50% maximal removal of NO_x. The preference of the reducing fuels for oxygen limits the effectiveness of this process for gas streams rich in O₂. Also, the heat generated by oxidation of the fuels makes heat recovery a must for economic viability.

SCR reduces NO_x to N₂ and H₂O over a catalyst bed with NH₃ as the reducing fuel. The optimum temperature range for this reaction is between 572 °F (300 °C) and 752 °F (400 °C). Strict temperature control minimizes the production of ammonium nitrates as well as ammonia oxidation. A 1:1 stoichiometric ratio of NO_x to ammonia can give up to 90% NO_x removal with minimal ammonia slip.

SNCR reduces NO_x with urea or ammonia as the reducing agent. Elevated temperatures, compared to SCR, make reaction in the absence of a catalyst possible. The lack of a catalyst and the elevated temperatures cause the production of some unwanted products, namely NO and N₂O.

Research and industry have made available a number of different catalyst varieties. Vanadium supported on Titania (V₂O₅/TiO₂) currently represents the most popular catalyst choice for SCR applications.

Research has shown that the reaction order with respect to ammonia is zero for the SCR reactions over a V₂O₅/TiO₂ catalyst due to fast binding of the ammonia to the surface. The rate-limiting steps are the reaction of NO with bound ammonia and the chemisorption of O₂ on the surface. The presence of water hinders SCR reactions by reversing the binding of O₂ to the surface of the catalyst.

We focus on a case study system located at the Radford Facility and Army Ammunition Plant (RFAAP) located in Radford, Virginia. The system combines extended absorption with SCR for the reduction of NO_x.

Many compounds compose the substance known as NO_x. Although NO and NO₂ represent the bulk of NO_x, N₂O₃ and N₂O₄ also exist in chemical equilibrium in a mixture of

NO_x at ambient conditions. In the presence of water, NO_x species react to form nitrous and nitric acids (HNO₂ and HNO₃ respectively). NO_x absorption proceeds through an extremely complex network of reactions and mass-transfer processes. For this reason, the usual optimization heuristics for gas-absorption units may be disappointing when applied to NO_x. A mechanistic model, solved with the help of computer simulation, proves the best course of action.

2.7 Nomenclature

CH ₄	methane
CO	carbon monoxide
EPA	Environmental Protection Agency
FUG	Fenske-Underwood-Gilliland
H ⁺	hydrogen ion
H ₂	hydrogen
H ₂ O	water
H ₂ O ₂	hydrogen peroxide
HNO ₂	nitrous oxide
HNO ₃	nitric acid
mol/L	moles per liter
N ₂	atmospheric nitrogen
N ₂ O	nitrous oxide
N ₂ O ₃	dinitrogen trioxide, product of NO + NO ₂
N ₂ O ₄	dinitrogen tetroxide, product of NO ₂ + NO ₂
NH ₃	ammonia
NO	nitric oxide
NO ₂	nitrogen dioxide
NSCR	non-selective catalytic reduction
O ₂	oxygen
SNCR	selective non-catalytic reduction
SO _x	sulfur oxide
SO ₂	sulfur dioxide
V ₂ O ₅ /TiO ₂	titania

2.8 References

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