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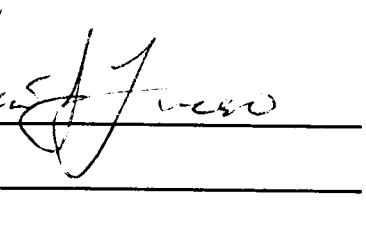
Signature 

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ABSORPTION OF NITROGEN OXIDES INTO AQUEOUS SODIUM HYDROXIDE SOLUTIONS

A Thesis

Presented for the

Master of Science

Degree

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Andrew J. Lucero

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ABSTRACT

The scrubbing of dilute gaseous nitrogen oxides into aqueous sodium hydroxide solutions has been studied using a pilot plant featuring an absorber packed with 1/2" Intalox saddles. The scrubbing efficiencies for dilute mixtures of NO and NO_2 were observed to dramatically increase when caustic solutions were used as the absorbent.

Three absorption models were tested in an attempt to explain the absorption of mixtures of dilute nitrogen oxides into caustic solutions in an absorber packed with 13-mm Intalox saddles. These models were first tested by finding values of $(\sqrt{Dk}/H)_{N_2O_4}$ and $(\sqrt{Dk}/H)_{N_2O_3}$ that allowed the three models to best fit the data.

The second phase of testing involved using each of the models to predict scrubbing efficiencies. Predictions from a model based on the absorption/hydrolysis of N_2O_4 and N_2O_3 agree well with experimental data.

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NOTATION

a	interfacial area per volume of tower
D	diffusion coefficient
g	gas
G	mass velocity of all gas
G^1	molar velocity of gas
H	phase distribution coefficient, for gas phase systems $H = P/C$
k	pseudo first order reaction rate constant
k_1, k_2, k_4	second order reaction rate constants
k_G	gas-phase mass-transfer coefficient
k_L	liquid-phase mass-transfer coefficient
K_i	pressure equilibrium constant of reaction i for the stoichiometry as written
L	mass velocity of liquid
L^1	molar velocity of liquid
l	liquid
N	absorption rate per interfacial area
P_A	partial pressure of component A
y_A	$= P_A/\pi$, mol fraction of A in gas
Z	height

SUBSCRIPTS

i	interfacial
in	entering
out	exiting
w	water
0	zero ionic strength

INTRODUCTION

Nitrogen oxides have been recognized as an important air pollution species. Their control is required by existing federal air quality standards (Federal Register, 36, No. 84, Part II, April 30, 1971, pp. 8186-8201). The absorption of nitrogen oxides is of significant industrial concern. Gaseous nitrogen oxides are produced from sources such as nitric acid production and storage, metal plating and finishing, and metal dissolution.

Gaseous nitrogen oxides are actually a mixture of several components; the most significant include NO, NO_2, N_2O_3, N_2O_4, and HNO_2. Since several reactions between these components occur in both the gas phase and the liquid phase, the absorption phenomena becomes increasingly complex. The nitrogen oxides become more difficult to remove in water scrubbers at low gaseous concentrations, and more so if the mixture contains substantial amounts of NO.

Scrubbing of gaseous nitrogen oxides has been studied at the Research Triangle Institute using a pilot plant absorber featuring a caustic solution as the absorbent. The study was conducted using an absorber packed to a height of 83 cm with 13 mm Intalox saddles. Nitrogen oxides removal efficiencies were obtained for inlet gas mixture concentrations varying from approximately 1000 ppm to 10000 ppm. Scrubber solutions of caustic concentrations varying from .25 to 25 weight percent NaOH were used for the absorbents. During these runs the $NO:NO_x$ ratio was varied from .07 to .37.

To describe the absorption phenomena, absorption flux models involving a two film theory approach were developed. Three absorption flux models were tested; the first provided for absorption of N_2O_4 and N_2O_3, the second for absorption of N_2O_4, N_2O_3, and NO_2, the third for absorption of N_2O_4, N_2O_3, and HNO_2. The model predictions for the first two models agree well with experimental results and literature values. Model 3 consistantly overpredicted absorption efficiencies by wide margins, many times predicting 100% NO_x removal.

BACKGROUND

The absorption of nitrogen oxides is an important industrial process. Nitrogen oxides (NO_x) cover all the positive oxidation states of nitrogen. Treatment of this multicomponent system can be simplified through the definition of "chemical NO," NO^*, and "chemical NO_2," NO_2^*. NO^* is defined as NO in any form; NO_2^* is defined as NO_2 in any form; and NO_x is the sum of the two; these quantities are defined as:

$$NO^* = NO + N_2O_3 + 1/2\ HNO_2 \quad (1)$$

$$NO_2^* = NO_2 + 2N_2O_4 + N_2O_3 + 1/2\ HNO_2 \quad (2)$$

$$NO_x = NO^* + NO_2^* \quad (3)$$

Since the absorption of NO_x into caustic solutions is expected to be similar to the absorption into water, much of the information available about NO_x scrubbing into water should apply. The theory of combined absorption and chemical reaction (Danckwerts, 1970) has been widely used to understand this system.

The reactions expected to be important in the gas phase are:

$$NO + 1/2\ O_2 \rightarrow NO_2 \quad (4)$$

$$2\ NO_2 \leftrightarrow N_2O_4 \quad (5)$$

$$NO + NO_2 \leftrightarrow N_2O_3 \quad (6)$$

$$NO + NO_2 + H_2O \leftrightarrow 2\ HNO_2 \quad (7)$$

The oxidation of NO to NO_2 occurs as an overall third order reaction (Bodenstein and Boes, 1922). Reactions (5), and (6) are considered to be fast and will be assumed to always be at equilibrium (Counce, 1980; Caudle and Denbigh, 1953). We are not too sure about (7); literature reaction rates vary widely. Hisatsune (1961), Hoftyzer and Kwanten (1972), and Forsythe and Giaque (1942) have established equilibrium constants for reactions (5), (6), and (7) respectively. The rate of reaction (4) can be described by the equation:

$$r_4 = k_4 P^2_{NO} P_{O_2} \tag{8}$$

Reactions (5), (6) and (7) are described by the following equations:

$$P_{N_2O_4} = K_5 P^2_{NO_2} \tag{9}$$

$$P_{N_2O_3} = K_6 P_{NO} P_{NO_2} \tag{10}$$

$$P_{HNO_2} = (K_7 P_W P_{NO} P_{NO_2})^{1/2} \tag{11}$$

The equilibrium constants can be expressed as functions of temperature.

$$K_5 \ (atm^{-1}) = 5.94 \times 10^{-10} \exp (6891.61/T) \tag{12}$$

$$K_6 \ (atm^{-1}) = 6.615 \times 10^{-8} \exp (4740/T) \tag{13}$$

$$K_7 \ (atm^{-1}) = 1.87 \times 10^{-7} \exp (4723/T) \tag{14}$$

An important consideration in the preceding set of reactions is the solubility of each of the NO_x and HNO_x specie. The solubilities play an important role in the design of the absorption equipment and processes. Henry's law is generally assumed to describe the equilibrium gas and liquid phase concentrations for this system.

$$H_A = P_A/C_A \tag{15}$$

The equilibriums ranked from least to most soluble are:

$$NO(g) \leftrightarrow NO(1) \tag{16}$$

$$NO_2(g) \leftrightarrow NO_2(1) \tag{17}$$

$$N_2O_3(g) \leftrightarrow N_2O_3(1) \tag{18}$$

$$N_2O_4(g) \leftrightarrow N_2O_4(1) \tag{19}$$

$$HNO_2(g) \leftrightarrow HNO_2(1) \tag{20}$$

$$HNO_3(g) \leftrightarrow HNO_3(1) \tag{21}$$

The Henry's law constants are presented in Table 1. These solubilities may be corrected for increased ionic strength according to the equation:

$$\log (H/H_0) = hI \tag{22}$$

where I is the ionic strength and h is calculated using values from Tables 2 and 3 from the equation (Sherwood, Pigford, and Wilke, 1975):

$$h = h_+ + h_- + h_g \tag{23}$$

Table 1. Henry's law constants at 298K

Species	H_i(m^3 atm/kg mol)
NO	518.0[a]
NO_2	142.7[b]
N_2O_3	2.59[c]
N_2O_4	.769[d]
HNO_2	.01667[e]
HNO_3	- - -

[a]Loomis (1928)

[b]Lee and Schwartz (1981)

[c]Corriveau (1971)

[d]Kramers, Blind, and Snoeck (1961)

[e]Park and Lee (1986)

Table 2. Ionic Strength Constants for Ions

Cations		Anions	
H^+	$h_+ = 0.0001\ m^3/kgion$	OH^-	$h_- = 0.066\ m^3/kgion$
N_a^+	0.091	Cl^-	0.021
K^+	0.074	NO_3^-	- 0.001
NH_4^+	0.028	SO_4^{--}	0.022
M_g^+	0.051	Br^-	0.012
Z_n	0.048	CO_3^{--}	0.021
C_a^{++}	0.053	I^-	0.005

Table 3. Constants for Dissolved Gases
Values of h_G m^3/kgion

Gas	Temperature, deg. C				
	0	15	25	40	60
H_2	--	-0.008	-0.002	--	--
O_2	--	0.034	0.022	--	--
CO_2	-0.007	-0.010	-0.019	-0.026	-0.016
N_2O	--	0.003	0.000	--	--
H_25	--	--	-0.033	--	--
NH_3	--	--	-0.054	--	--
C_2H_2	--	--	-0.009	--	--
SO_2	--	--	-0.013	--	--

Several reactions occur when nitrogen oxide mixtures are scrubbed with water.

$$N_2O_4(1) + H_2O(1) \rightarrow HNO_2(1) + HNO_3(1) \quad (24)$$

$$N_2O_3(1) + H_2O(1) \rightarrow 2HNO_2(1) \quad (25)$$

$$3NO_2(g) + H_2O(1) \leftrightarrow 2HNO_3(1) + NO(g) \quad (26)$$

Rate constants for reactions (24) and (25) have been established by Kramers, Blind, and Snoeck (1961) and by Corriveau (1971). Reaction (26) may be visualized as an overall reaction which can be separated into a series of reactions. Equation (26) may be broken down to

$$2NO_2(g) \leftrightarrow N_2O_4(g) \quad (27)$$

$$N_2O_4(g) \leftrightarrow N_2O_4(1) \quad (28)$$

$$N_2O_4(1) + H_2O(1) \leftrightarrow H^+(1) + NO_3\text{-}(1) + 2HNO_2(1) \quad (29)$$

$$3HNO_2(1) \leftrightarrow H^+(1) + NO_3(1) + H_2O(1) + 2NO(1) \quad (30)$$

$$NO(1) \leftrightarrow NO(g) \quad (31)$$

Since the hydrogen ion would be neutralized by the presence of the hydroxide ion, the reaction series would be stopped with reaction (29). N_2O_4 and N_2O_3 could also react directly with the hydroxide ion according to the following (Carta, 1984).

$$N_2O_4(l) + 2OH^-(l) \rightarrow NO_2^-(l) + NO_3^-(l) + H_2O\ (l) \quad (32)$$

$$N_2O_3(l) + 2OH^-(l) \rightarrow 2NO_2^-(l) + H_2O(l) \quad (33)$$

The reverse of reactions (29) and (30) would be prevented in the presence of the hydroxide ion.

Researchers have confirmed that the rate controlling step for the absorption of NO_x into water is the absorption-hydrolysis of N_2O_4 and of N_2O_3 (Corriveau, 1971; Hoftyzer and Kwanten, 1972).

In the absence of NO^* and at very low gaseous concentrations of NO_2^*, the absorption of N_2O_4 becomes less important and the absorption of molecular NO_2 apparently becomes the dominant route (Lee and Schwartz, 1981; Komiyama and Inoue, 1980; Selby and Counce, 1986).

$$NO_2(g) \leftrightarrow NO_2(l) \quad (34)$$

$$2NO_2(l) + H_2O(l) \leftrightarrow H^+(l) + NO_3^-(l) + HNO_2(l) \quad (35)$$

There is much disagreement concerning the role of HNO_2 in the absorption of NO_x. Studies by Counce and Perona (1983) and by Corriveau with water scrub solution (1971) did not support mechanisms of gas phase formation and absorption of HNO_2. Work by Carta (1984) and Newman and Carta (1987) indicates that when caustic solutions are used, HNO_2 may be formed and absorbed. This mechanism may be represented by:

$$NO_2(g) + NO(g) + H_2O(g) \leftrightarrow 2HNO_2(g) \quad (36)$$

$$HNO_2(g) \leftrightarrow HNO_2(l) \quad (37)$$

$$HNO_2(l) + OH^-(l) \rightarrow NO_2^-(l) + H_2O(l) \quad (38)$$

From the film theory for mass transfer with combined chemical reaction, the flux equations are:

$$N_a = k_G(P_a - P_{a,i}) \tag{39}$$

for the gas phase and

$$N_a = E_a k_L(C_{a,i} - C_A) \tag{40}$$

for the liquid phase.

The enhancement factor is determined by the kinetics of the chemical reaction. For a fast pseudo-first order reaction, the enhancement factor becomes:

$$E_a = \sqrt{D_a k}/k_L \tag{41}$$

Substituting Henry's law for the concentrations and assuming fast pseudo-first order liquid-phase absorption flux equations become:

$$N_{N_2O_4} = 2(\sqrt{Dk}/H)_{N_2O_4} P_{N_2O_4,i} \tag{42}$$

and

$$N_{N_2O_3} = (\sqrt{Dk}/H)_{N_2O_3} P_{N_2O_3,i} \tag{43}$$

Several researchers found that the rate of absorption of NO_2-N_2O_4 mixtures actually decreased when NaOH was used as the absorbent (Chambers and Sherwood, 1937; Caudle and Denbigh, 1953; Peters and Holman, 1955; Chilton and Knell, 1972). This effect has been

attributed to the decrease in solubility caused by the presence of the NaOH. Kameoka and Pigford (1977) noted an increase in the rate of absorption working with a more dilute NaOH solution and proposed the following equation to describe the effect:

$$N_{N_2O_4} = (\sqrt{D(k_1 C_{H_2O} + k_2(C_{OH^-})})_{N_2O_4} P_{N_2O_4,i} \quad (44)$$

If HNO_2 is formed in the gas phase and absorbed, the enhancement factor for the absorption of this component becomes:

$$E_{HNO_2} = 1 + D_{OH^-} C_{OH^-} / D_{HNO_2} C_{HNO_2,i} \quad (45)$$

Reported values of $(\sqrt{Dk}/H)_{N_2O_4}$ in the literature range from 9.03×10^{-5} (Hoftyzer and Kwanten, 1972) to 1.1×10^{-3} kmole/m^2atm sec (Gerstacker, 1961). Kameoka and Pigford (1977) found that the $(\sqrt{Dk}/H)_{N_2O_4}$ for absorption into NaOH solutions was described by the form:

$$(D(k_1 C_{H_2O} + k_2 C_{OH^-}))^{1/2}$$

where $k_1 C_{H_2O} = 194 \text{ sec}^{-1}$

and $k_2 = 147 \text{ m}^3/\text{kgion sec.}$

Aoki et al. (1982) found a value of .104(kmol/m^2atm sec) for $(\sqrt{Dk}/H)_{N_2O_3}$ in aqueous NaOH solutions, and Newman and Carta (1987) reported a value of .025 (kmole/m^2atm sec).

MATHEMATICAL MODEL

Three mathematical models are proposed in this research to attempt to describe the observed experimental results. These models will be based on the concept of gas and liquid mass-transfer films to describe the mass transfer coupled with simultaneous chemical reaction. The first is based on the absorption of N_2O_4 and N_2O_3; the second is based on the absorption of N_2O_4, N_2O_3, and NO_2; the third on the absorption of N_2O_4, N_2O_3, and HNO_2. The earlier definitions of NO_2^* and NO^* allow the multicomponent gas-phase flux to be treated as a bicomponent flux of NO^* and NO_2^*; the resulting flux equations for model 1 are:

$$N_{NO_2}{}^* = k_G(P_{NO_2}{}^* - P_{NO_2}{}^*{}_{,i} \tag{46}$$

$$N_{NO}{}^* = k_G(P_{NO}{}^* - P_{NO}{}^*{}_{,i}) \tag{47}$$

for the gas phase and

$$N_{NO_2}{}^* = 2(\sqrt{Dk}/H)_{N_2O_4} K_5 P^2{}_{NO_2}{}^*{}_{,i} + (\sqrt{Dk}/H)_{N_2O_3} K_6 P_{NO}{}^*{}_{,i} P_{NO_2}{}^*{}_{,i} \tag{48}$$

$$N_{NO}{}^* = (\sqrt{Dk}/H)_{N_2O_3} K_6 P_{NO_2}{}^*{}_{,i} P_{NO}{}^*{}_{,i} \tag{49}$$

for the liquid phase.

The respective k's in these equations may be considered a combination of the second order rate constants from reactions 24, 25, 32, and 33 ($k_1 C_{H_2O} + k_2 C_{OH^-}$).

The second model involves the addition of an incremental flux of NO_2^* due to the absorption and slow hydrolysis of molecular NO_2 to equation (48).

$$\Delta N_{NO_2}{}^* = (k_L/H)_{NO_2} P_{NO_2,i} \tag{50}$$

The third model adds an incremental flux of NO_2^* and NO^* due to the absorption of HNO_2 and accompanying instantaneous reaction

$$\Delta N_{NO_2}{}^* = \Delta N_{NO}{}^* = 1/2\ k_G(K_7 P_w P_{NO}{}^* P_{NO_2}{}^*)^{1/2} \tag{51}$$

to equations (39) and (40).

These flux equations are then related to the differential material balances according to the equations:

$$G^1\ d\ Y_{NO_2^*} = N_{NO_2^*}\ a\ dZ \tag{52}$$

$$G^1\ d\ Y_{NO^*} = N_{NO^*}\ a\ dZ \tag{53}$$

These equations may be solved numerically by approximating the integral as a series of Z increments.

$$G^1\ \Delta Y_{NO_2^*} = N_{NO_2^*}\ a\ \Delta Z \tag{54}$$

$$G^1\ \Delta Y_{NO^*} = N_{NO^*}\ a\ \Delta Z \tag{55}$$

Equations (46), (47), (48), and (49) may be simultaneously solved for each ΔZ element through the column. The assumptions required to develop this model are:

1. The column operates as a plug flow absorber with respect to gas and liquid flow.

2. The gases behave ideally.

3. Oxidation of NO to NO_2 is negligible. (Equation 4 is neglected.)

4. Reactions 5, and 6 are in equilibrium and apply at all times in the bulk gas phase.

5. Reactions 5, and 6 apply in the gas mass-transfer film.

6. The absorption of N_2O_3 and N_2O_4 occurs in the fast-pseudo-first-order reaction regime.

7. Liquid composition remains essentially constant throughout the column.

Values for k_G, a, and k_L are available from correlations in the literature. Although several values for $(\sqrt{Dk}/H)_{N_2O_4}$ and $(\sqrt{Dk}/H)_{N_2O_3}$ are available in the literature for absorption into water, values for absorption into NaOH are not as numerous.

The model was tested in two ways. Since the values for $(\sqrt{Dk}/H$ are not as well known for absorption into NaOH, the model was first tested by using the actual inlet and exit NO_x concentrations to optimize the coefficients for $(\sqrt{Dk}/H)_{N_2O_4}$ and for $(\sqrt{Dk}/H)_{N_2O_3}$. These coefficients were then compared to literature values.

Initial guesses for the mass transfer coefficients were generated assuming a log-mean driving force.

$$P_{NO_2^*} = (P_{NO_2^*,in} - P_{NO_2^*,out}) / \log (P_{NO_2^*,in}/P_{NO_2^*,out}) \quad (56)$$

$$P_{NO^*} = (P_{NO^*,in} - P_{NO^*,out}) / \log (P_{NO^*,in}/P_{NO^*,out}) \quad (57)$$

Actual fluxes can then be directly calculated from the experimental data by rearranging equations (54) and (55).

$$N_{NO_2^*} = (P_{NO_2^*,in} - P_{NO_2^*,out}) \; G(aZRT) \quad (58)$$

$$N_{NO^*} = (P_{NO^*,in} - P_{NO^*,out}) \; G(aZRT) \quad (59)$$

The concentrations of NO^* and NO_2^* at the interface can then be calculated by rearranging equations (46) and (47).

$$P_{NO_2^*,i} = P_{NO_2^*} - N_{NO_2^*}/k_{G,NO_2^*} \quad (60)$$

$$P_{NO^*,i} = P_{NO^*} - N_{NO^*}/k_{G,NO^*} \quad (61)$$

The liquid phase mass transfer coefficients can then be calculated from equations (48) and (49).

$$(Ek_L/H)_{N_2O_3} = N_{NO^*}/(K_6 P_{NO^*,i} P_{NO_2^*,i}) \quad (62)$$

$$(Ek_L/H)_{N_2O_4} = (N_{NO_2^*} - N_{NO^*})/(K_5 P_{NO_2^*,i}^2) \quad (63)$$

These coefficients were tested by using equations (54) and (55) to calculate the exit concentrations and scrubbing efficiencies. If the calculated NO^* and NO_2^* scrubbing efficiencies were not within 5% of the actual efficiencies, the coefficients were adjusted.

For the second model the numerator in equation (63) becomes $N_{NO_2}^* - N_{NO}^* - (k_L/H)_{NO_2} P_{NO}^*,_i$. The enhancement factor is then checked to determine whether the reaction still occurs in the fast regime. For a fast reaction the film conversion parameter is tested against the enhancement factor for instantaneous reaction.

$$1/2\ E_i > M > 3 \tag{64}$$

$$M = D_{N_2O_4}\ k_{32}\ C_{OH^-}/k_L^2 \tag{65}$$

$$E_i = 1 + D_{OH^-}\ C_{OH^-}/(2\ D_{N_2O_4}\ C_{N_2O_4,i}) \tag{66}$$

Similar tests can be conducted for N_2O_3.

$$M = D_{N_2O_3} k_{33}\ C_{OH^-}/k_L^2 \tag{67}$$

$$E_i = 1 + D_{OH^-}\ C_{OH^-}/(2\ D_{N_2O_3} C_{N_2O_3,i}) \tag{68}$$

If the inequality in equation (64) holds, the enhancement factor E in equations (62) and (63) becomes $\sqrt{M}$ (Levenspiel, 1972).

The third model involves the addition of an incremental flux of HNO_2 according to equation (51). The absorption of HNO_2 is modelled as absorption followed by an instantaneous reaction. This model also involves a test to determine the form of the flux equation.

If

$$k_G P_{HNO_2} < k_L D_{OH^-}\ C_{OH^-}/D_{HNO_2} \tag{69}$$

then

$$N_{HNO_2} = k_G P_{HNO_2}. \tag{70}$$

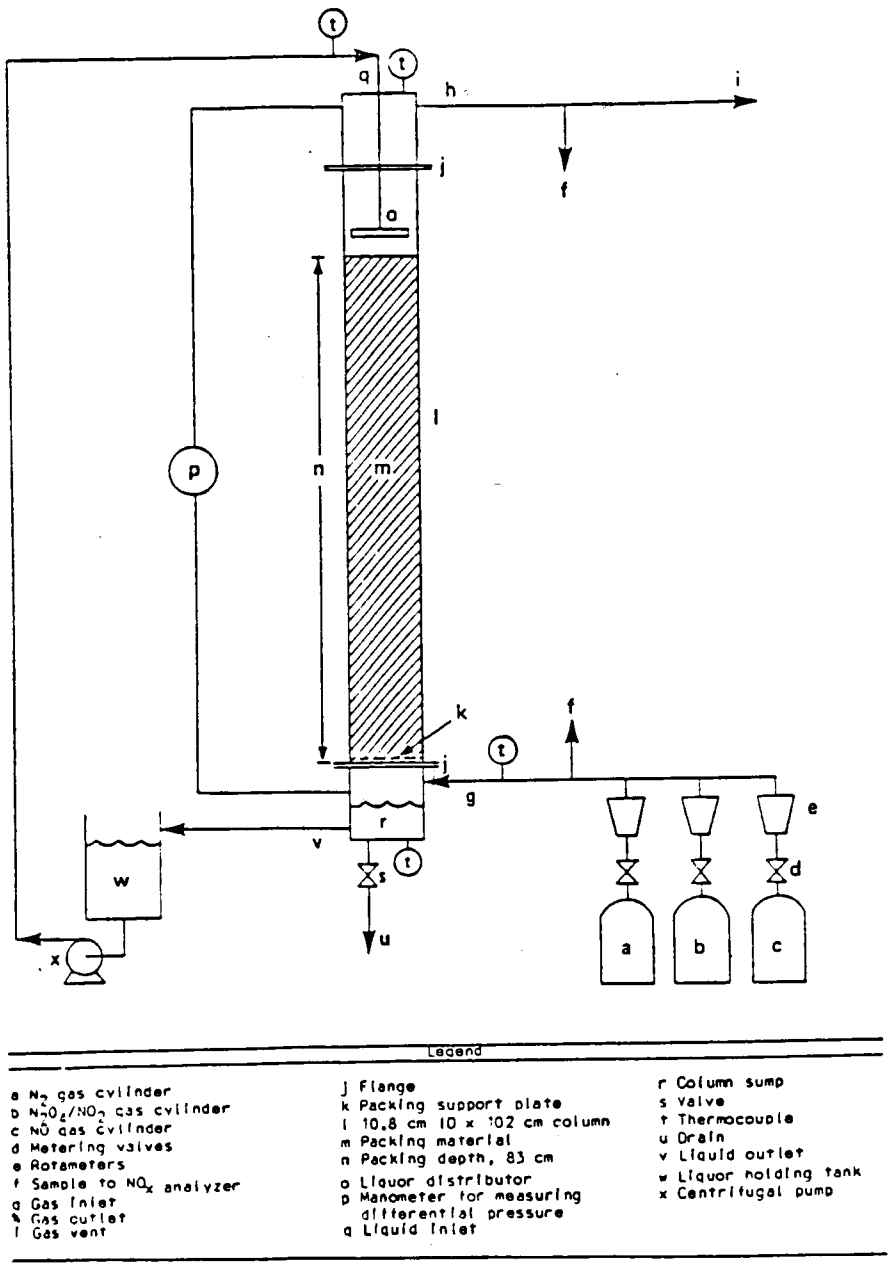
The second phase of modelling involves predicting the outlet concentrations by substituting equations (46) through (49) into (54) and (55) to integrate through the tower to predict the outlet NO_x concentrations.

EXPERIMENTAL

The experimental investigation was conducted by the Research Triangle Institute. The scrubber was constructed of plexiglass with a length of (40"), an inner diameter of (4 1/4"), and a packing height of (33"). Tests were conducted using (1/2") Ceramic Intalox Saddles, (5/8") Polypropylene Flexirings, and Type BX Sulzer packing. Only the Ceramic Intalox tests were used to optimize the (Dk/H) parameters. The scrubber is shown schematically in Figure 1. Inlet NO_x concentrations were varied from 1000 to 12000 ppm, but most of the experiments were conducted with NO_x concentrations between 3000 and 5000 ppm.

The experiments were run using gas flow rates of 1, 4, and 8 (CFM); and liquid flow rates of .5 and 1.0 (GPM). The resulting mass-based nondimensional L/G ratios ranged from 15 to 120. The caustic concentration was varied from zero to 25 wt %.

Liquid flow rates were measured by triplicate recording of the time required to fill a container of known volume, and gas flow rates measured by a previously calibrated rotameter. Concentrated caustic (25 wt %) was prepared by the addition of reagent grade NaOH to measured volumes of deionized water. Reduced concentrations were prepared by diluting the concentrated solution. Samples of the caustic solutions were periodically titrated to confirm the nominal concentrations.



Legend

a N_2 gas cylinder
b N_2O_4/NO_2 gas cylinder
c NO gas cylinder
d Metering valves
e Rotameters
f Sample to NO_x analyzer
g Gas inlet
h Gas outlet
i Gas vent
j Flange
k Packing support plate
l 10.8 cm ID x 102 cm column
m Packing material
n Packing depth, 83 cm
o Liquor distributor
p Manometer for measuring differential pressure
q Liquid inlet
r Column sump
s Valve
t Thermocouple
u Drain
v Liquid outlet
w Liquor holding tank
x Centrifugal pump

Figure 1. Schematic of RTI NO_x Scrubber (Sickles and Harkins, 1985)

Inlet and exit NO and NO_2 concentrations were determined using a TECO Model 10 chemiluminescent NO_x analyzer. The analyzer was following each series. Experiments were conducted using two nominal NO_x levels: low (below 1500 ppm) and high (3000 to 5000 ppm); with two nominal NO levels: low and high. The experimental procedure is given in Table 4 and the experimental data are presented in Table 5.

Table 4. Experimental Procedure (Sickles and Harkins, 1985)

1.	Flush column and liquid system with tap water; rinse with deionized water; calibrate NO_x meter.
2.	Place scrubbing liquid into stainless steel storage tank.
3.	Activate pump; adjust and measure liquid flow rate.
4.	Activate N_2 flow; adjust flow rate.
5.	Add NO_2 to inlet gas; measure inlet NO_x.
6.	Add NO (if required) to inlet gas; measure inlet NO_x.
7.	Operate system for approximately 4 minutes.
8.	Measure inlet NO and NO_x.
9.	Measure outlet NO and NO_x.
10.	Remeasure inlet NO and NO_x.
11.	Remeasure outlet NO and NO_x.
12.	If duplicate measurements agree within 2%, stop collecting data; otherwise repeat measurements.
13.	Measure inlet and outlet gas temperatures, inlet and outlet liquid temperatures, column pressure drop, and pressure at the top of the column.
14.	Adjust N_2, NO_2 and NO for next test.
15.	Dilute scrubber liquid (if necessary).
16.	Return to step 7.

Table 5. Experimental Data

Run #	G_3 ($\frac{ft^3}{min}$)	L ($\frac{gal}{min}$)	OH^- (wt%)	NO in (ppm)	NO_2 in (ppm)	NO out (ppm)	NO_2 out (ppm)
1	4	1	25	290	1130	62	700
2	4	1	25	580	1320	56	730
3	4	1	25	400	2900	67	1750
4	4	1	25	1510	3130	110	1140
5	4	1	12	280	840	78	330
6	4	1	12	500	930	140	290
7	4	1	12	450	2890	170	1090
8	4	1	12	1500	3140	120	790
9	4	1	10	240	2990	140	1320
10	4	1	10	1790	3130	190	740
11	4	1	4	1890	3030	240	550
12	8	1	4	1880	3080	520	880
13	1	1	4	1880	3250	23	280
14	1	1	4	3360	6180	26	400
15	4	1	.25	1910	2980	520	550
16	4	1	8.1	320	810	76	370
17	4	1	8.1	500	1110	100	400
18	4	1	8.1	390	2960	170	1040
19	4	1	20	250	1100	64	660
20	4	1	20	650	910	210	410
21	4	1	20	380	2940	94	1550

Table 5. Experimental Data (continued)

Run #	G_3 $\left(\frac{ft^3}{min}\right)$	L $\left(\frac{gal}{min}\right)$	OH^- (wt%)	NO in (ppm)	NO_2 in (ppm)	NO out (ppm)	NO_2 out (ppm)
22	4	1	20	1490	3066	92	1110
23	4	1	15.2	250	840	50	560
24	4	1	15.2	520	840	140	460
25	4	1	15.2	440	2800	75	1410
26	4	1	15.2	1540	2750	97	970
27	4	1	8.1	1460	3160	126	780
28	4	1	4	140	1030	38	500
29	4	1	4	500	1090	76	430
30	4	1	4	350	3100	100	960
31	4	1	4	1410	3260	110	810
32	4	.5	4	1790	3020	230	540
33	1	.5	4	1750	3190	23	270
34	1	.5	4	3500	5910	26	290
35	4	1	4	280	3040	90	1110
366	4	1	4	1820	3050	200	630

RESULTS

Part of the objective for these experiments was to determine an optimum caustic concentration for absorbing NO_2. An unambiguous optimum caustic concentration could not be determined for the experiments shown in Figure 2 (high NO_x). The highest removal efficiencies did not occur with the highest concentrations of caustic or with water alone. The highest NO_x removal efficiencies for high NO^* levels occurred at caustic concentrations between 1 and 8 weight percent, but for the experiments with low NO levels, the best performance occurred at .5 weight percent caustic. Higher caustic concentrations tended to decrease the scrubber performance for the low NO^* experiments.

For all of the combinations of NO^*-NO_2^* tested, the actual caustic concentration did not exert a strong influence on the scrubbing efficiencies, thus permitting the comparison of efficiencies shown in Table 6. The mean removal efficiencies are much better with caustic solutions than with water alone. Increasing the ratio of NO^* to NO_2^* enhances the NO_x removal by caustic, but not by water. This effect is shown on Figure 3 and on the previously shown Figure 2.

In several experiments at 4% caustic, the liquid flow rate was halved from 1.0 to .5 GPM at a fixed gas flow rate. No influence on scrubber performance was observed, suggesting that the NO_x removal efficiencies are not sensitive to liquid flow rate in this range.

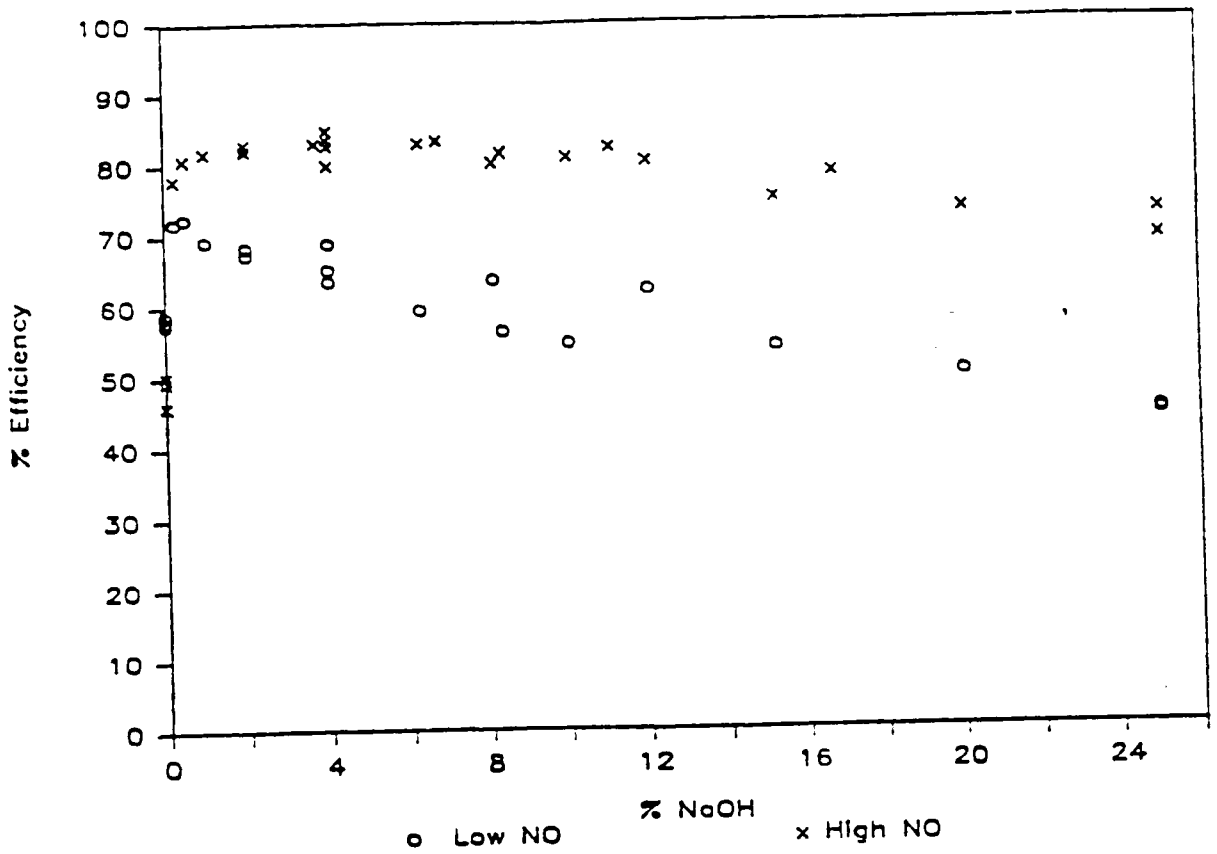


Figure 2. Experimental NO_x Scrubbing Efficiency for $NO^*:NO_2^*$ Ratios of 0.1 and 0.6 at Varying NaOH Concentrations (Sickles and Harkins, 1985)

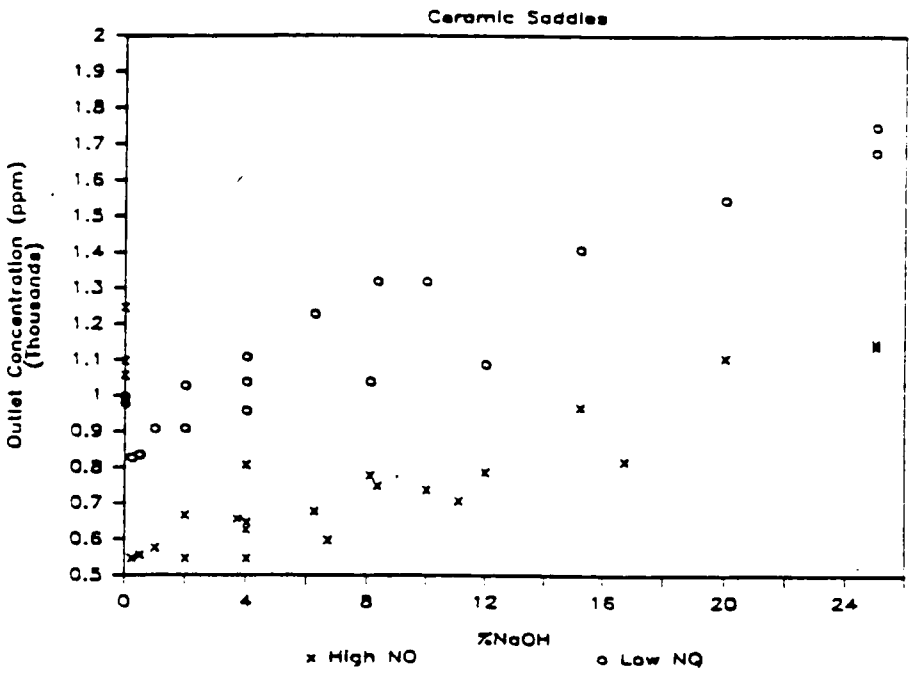


Figure 3. Outlet NO_2 Concentrations for Scrubbing Liquors of Various Caustic Concentrations in the RTI Scrubber with Ceramic Saddle Packing. Nominal Inlet NO_2 Level: 3100 ppm; Nominal Inlet NO: 1750 ppm (High) and 300 (Low) (Sickles and Harkins, 1985)

Table 6. NO_x Removal Efficiency With Caustic and With Water as Scrubbing Media for Various Combinations of NO and NO_x (Sickles and Harkins, 1985)

Concentration		Mean NO_x Removal Efficiency					
		Water			Caustic		
NO_x	NO	n	$\bar{X}$	SD	n	$\bar{X}$	SD
High	High	3	48.7	2.3	22	80.2	4.1
High	Low	3	58.3	0.6	17	61.4	9.0
Low	High	1	35.0	-	7	61.6	7.8
Low	Low	1	41.0	-	7	49.1	11.8

Experiments were also conducted to test the efficiency versus the L'/G' ratio. As shown in Figure 4, the efficiency tended to increase as the L'/G' ratio increased.

All efforts to model this system are highly dependent on the input parameters. The kinetic, equilibrium, and mass-transfer coefficients presented in Table 7 are thought to be the best estimates available.

Initial model testing proceeded by finding values for $(\sqrt{Dk}/H)_{N_2O_4}$ and $(\sqrt{Dk}/H)_{N_2O_3}$ that best allowed the respective models to fit the data for each experiment. These coefficients were then tested to verify the reaction regime.

The optimized parameters for Model 1 are shown in Figure 5 and Figure 6. The values for $(\sqrt{Dk}/H)_{N_2O_4}$ shown in Figure 5 appear to qualitatively agree with other experiment observations references, generally decreasing with increasing hydroxide concentration. These

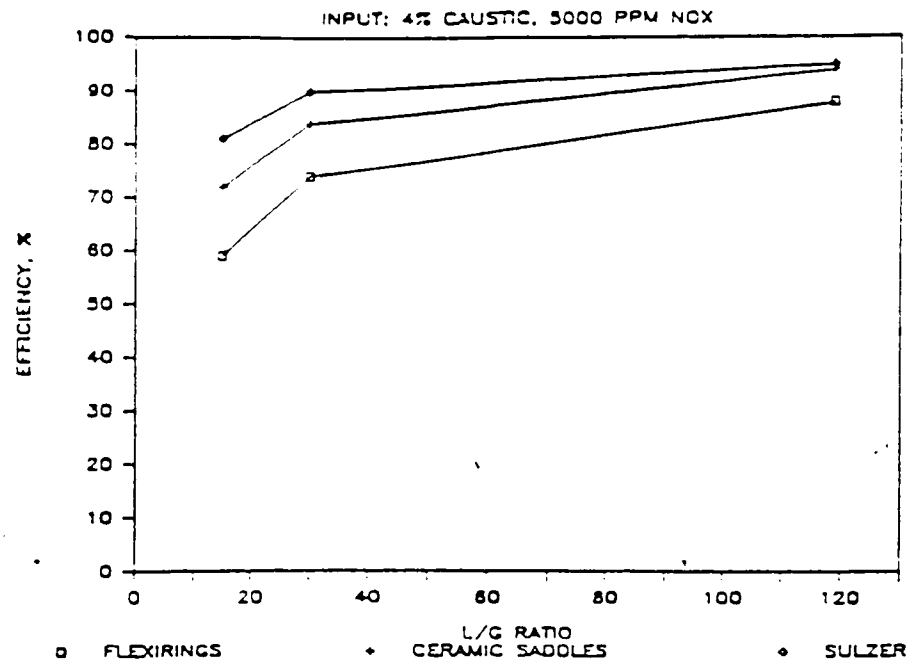


Figure 4. NO_x Removal Efficiency for 4% Caustic in RTI Scrubber at a Constant Liquid Flow Rate of 1 GPM as a Function of L'/G' Ratio for Three Packing Types: Sulzer, Ceramic Saddles, and Flexirings

Table 7. Source of Kinetic, Equilibrium and Mass-transfer Coefficients. 1987.

a	- Joshi, Mahajani, and Juvekar (1985)
H_{NO_2}	- Lee and Schwartz (1981)
k_G	- Joshi, Mahajani, and Juvekar (1985)
k_L	- Dankwerts (1970)
K_6	- Hisatsune (1961)
K_{11}	- Hoftijzer and Kwanten (1972)
K_{16}	- Hoftijzer and Kwanten (1972)
P_{H_2O}	- Perry, Chilton (1973)

coefficients appear to be within the range of reported literature values for absorption into water.

The optimized values for $(\sqrt{Dk}/H)_{N_2O_3}$ shown in Figure 6 exhibit little overall trend when plotted versus NaOH concentration. Figure 7 shows $(\sqrt{Dk}/H)_{N_2O_3}$ versus NO/NO_x ratio, showing no specific trend.

An average value for $(\sqrt{Dk}/H)_{N_2O_3}$ of .126 with a standard deviation of .057 compares well, however, with the value of 0.10 $kmol/m_2sec$ atm obtained by Aoki et al. (1982).

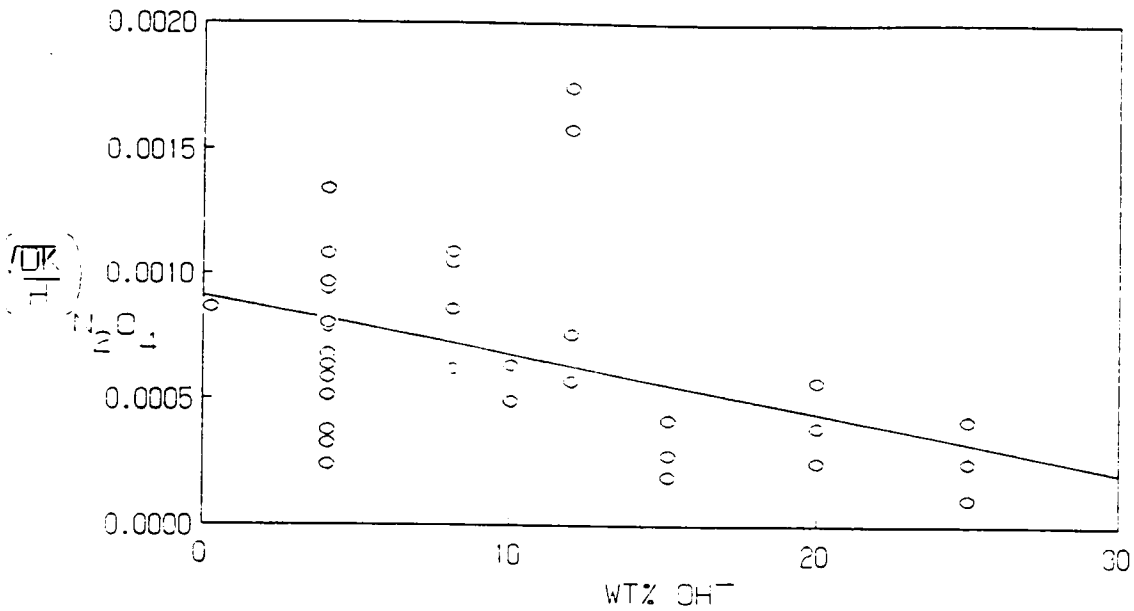


Figure 5. Optimized Values of $(\sqrt{Dk}/H)_{N_2O_4}$ for Model 1.

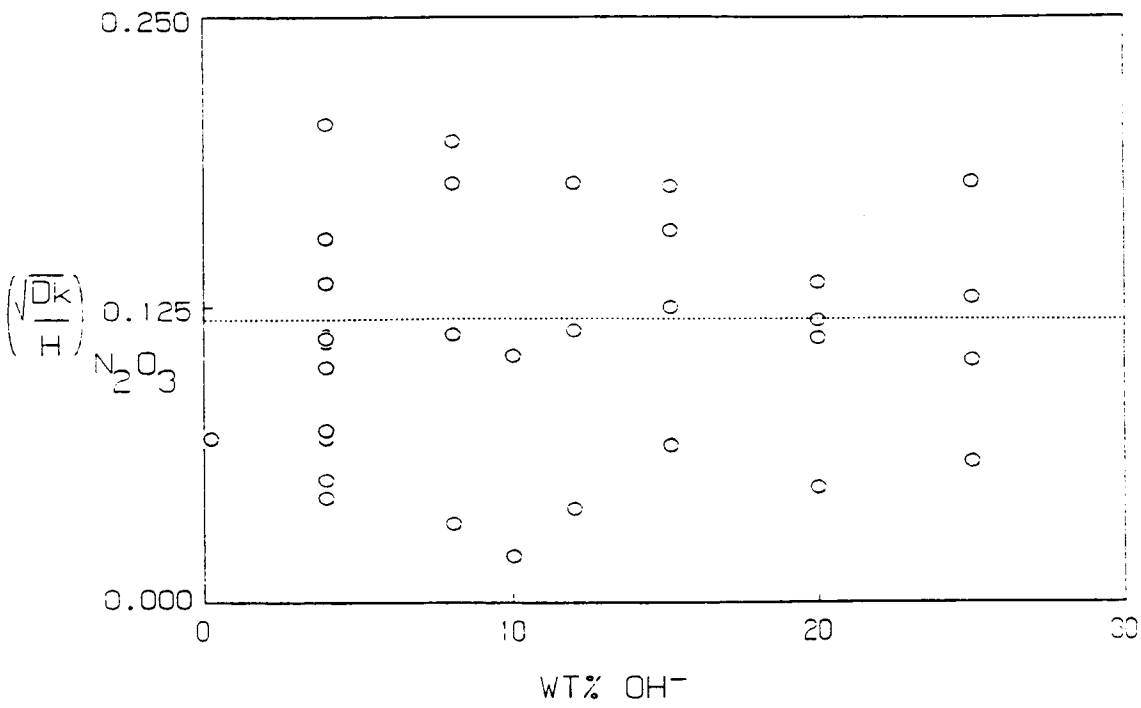


Figure 6. Optimized Values of $(\sqrt{Dk}/H)_{N_2O_3}$ for Model 1.

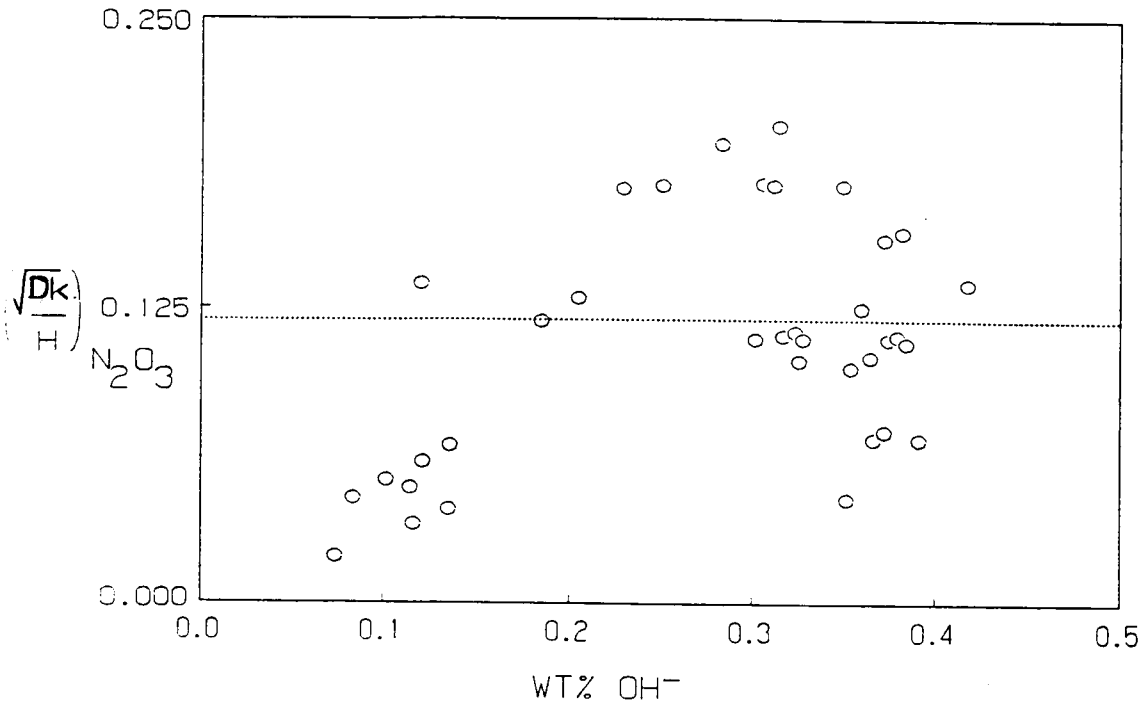


Figure 7. $(\sqrt{Dk}/H)_{N_2O_3}$ versus NO/NO_x Ratio

The coefficients for both $(\sqrt{Dk}/H)N_2O_3$ and $(\sqrt{Dk}/H)N_2O_4$ were then tested from equations (64) through (68) to check the assumption that the reactions occur in the fast regime. All of the coefficients for $(\sqrt{Dk}/H)_{N_2O_3}$ were found to fall well within the range described by equation (64). While the coefficients for $(\sqrt{Dk}/H)_{N_2O_4}$ also fall within the range of equation (64), they occur on the lower end of the inequality, and for many experiments barely fall in that range.

The coefficients obtained from the analysis of Model 2 are almost identical to those obtained from Model 1. This result is not unexpected since the absorption of NO_2 has been shown to be important only at very low concentrations of NO_2* (Lee and Schwartz, 1981; Selby and Counce, 1986).

The application of Model 3 is extremely sensitive to the value of k_G used. The flux of HNO_2 becomes the dominant absorption route, forcing $(\sqrt{Dk}/H)N_2O_3$ near zero. For the model input parameters used, Model 3 predicts much higher absorption fluxes than were experimentally observed. Due to uncertainty in the estimates of the model input parameters, this model cannot be completely ruled out.

To test the possibility of a mechanism other than the absorption of N_2O_3, the flux of NO^* is plotted versus P_{NO}^* $P_{NO_2}^*$ over on log-log coordinates. If the predominant absorption mechanism was the absorption of N_2O_3 as assumed, the plot should yield a line with a slope of 1. If the predominant mechanism was the absorption of HNO_2, the plot would yield a line with a slope of 1/2. A combination would give something in between. This plot is shown in Figure 8. The experiments with low nominal concentrations of both NO^* and NO_2^*, and

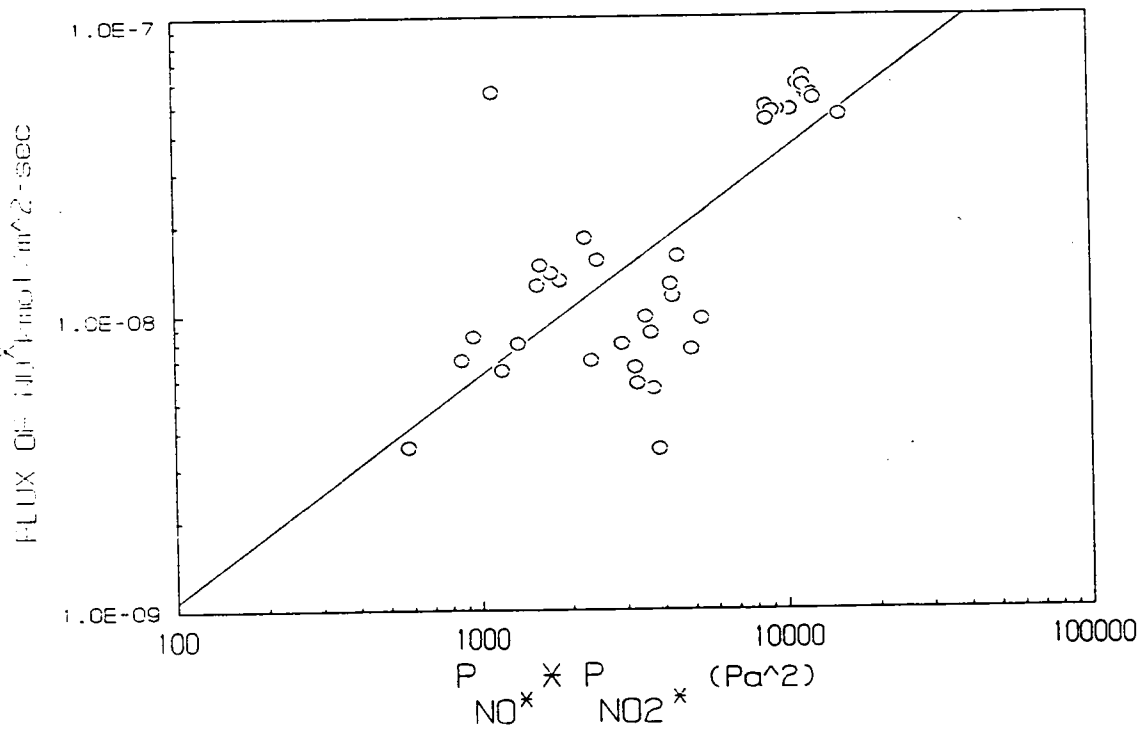


Figure 8. Pressure-Flux Diagram for NO^*

those with high nominal concentrations of both NO^* and NO_2^* seem to fall on the line with a slope of 1. The points with low NO^* concentrations and high NO_2^* concentrations do not fall on this line, possibly because of the dominance of the absorption of N_2O_4. Figure 9 shows a plot checking the absorption mechanism of NO_2^*. A log-log plot of $N_{NO_2}^* - N_{NO}^*$ versus $P_{NO_2}^*$ should give a line with a slope of 2. The points tend to scatter about this range.

The second phase of testing the models consisted of using the models to predict the exit NO_x concentrations from the inlet NO_x concentrations for each experiment using literature parameters for $(\sqrt{Dk}/H)$ for N_2O_3 and N_2O_4, Aoki et al. (1982) and Kameoka and Pigford (1977), respectively. Both Model 1 and Model 2 predicted the exit concentrations except for experiments that had low NO^*/NO_x ratios (low nominal concentration of NO^*, high nominal concentration of NO_2^*). At low NO^*/NO_x ratios, both models tended to overpredict the absorption efficiencies. As expected, the predictions of the two models differ very little. Figure 10 shows the error between the model prediction and the actual experimental data versus the NO/NO_x ratio.

Although the NO/NO_x ratio tended to affect the predicted efficiencies for Model 1, the actual NO_x inlet concentration had little effect on the predictions. Figure 11 shows the residuals versus the NO_x concentration. As shown in Figure 12, the model tended to predict efficiencies slightly better at the higher OH^- concentrations.

Model 3 predicted much higher absorption efficiencies than were experimentally observed for all points, and many times predicted 100%

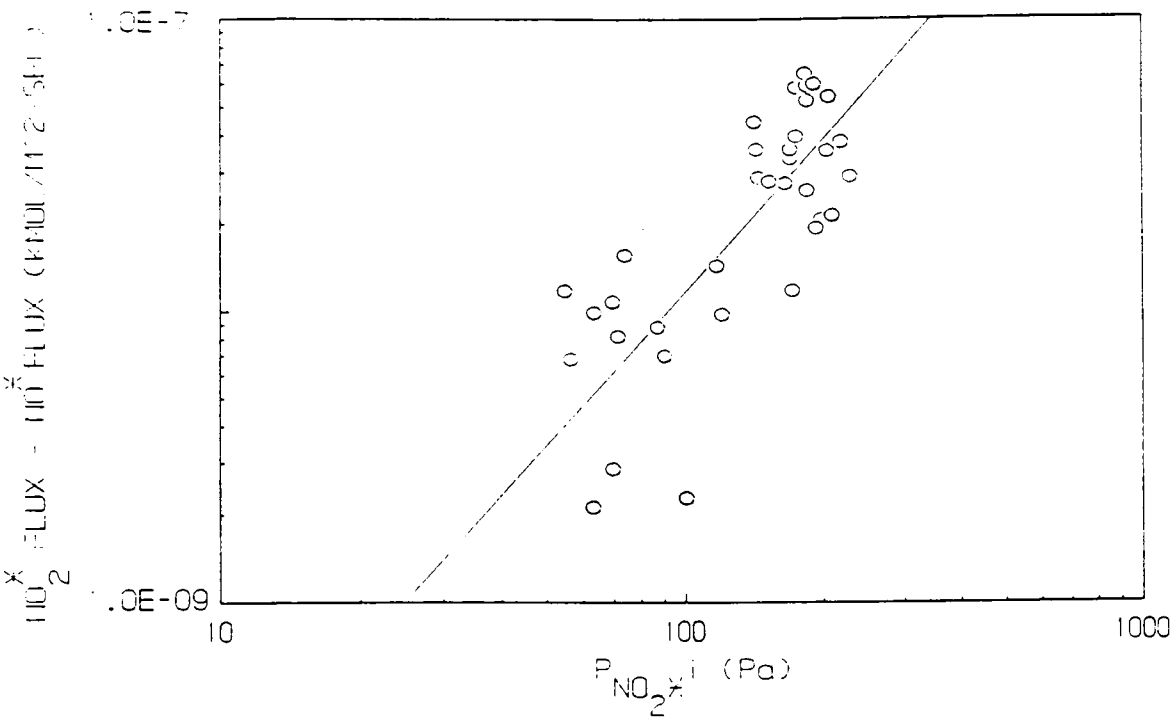


Figure 9. Pressure-Flux Diagram for NO_2^*

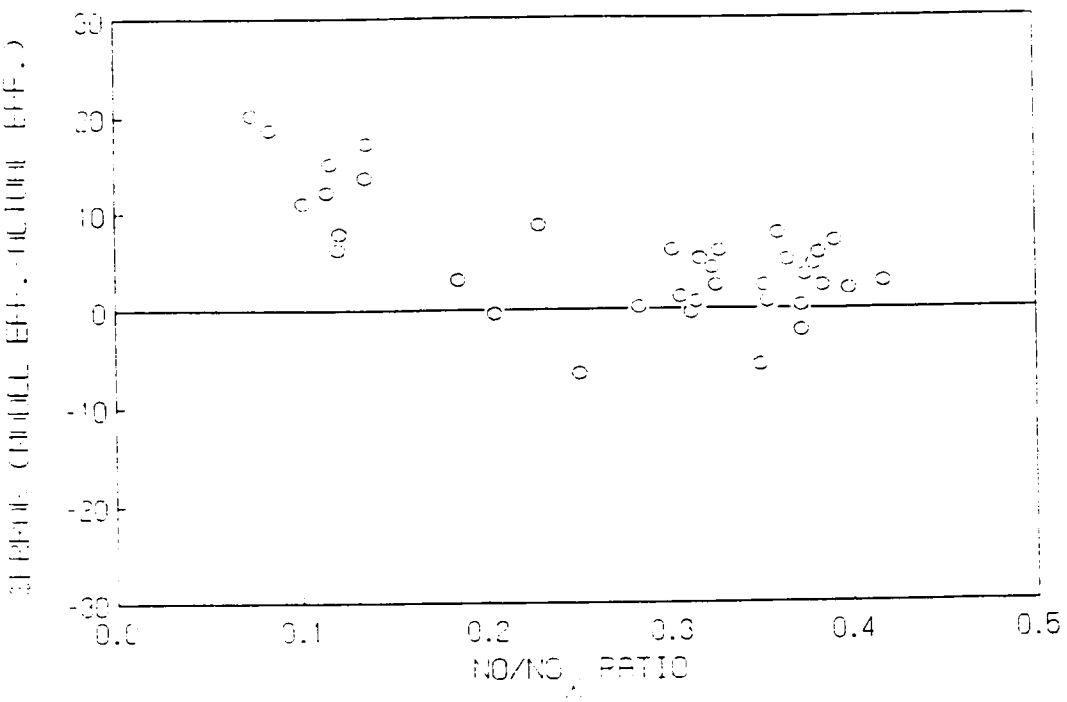


Figure 10. Residuals versus NO/NO$_x$ Ratio for Model 1 with Literature Parameters

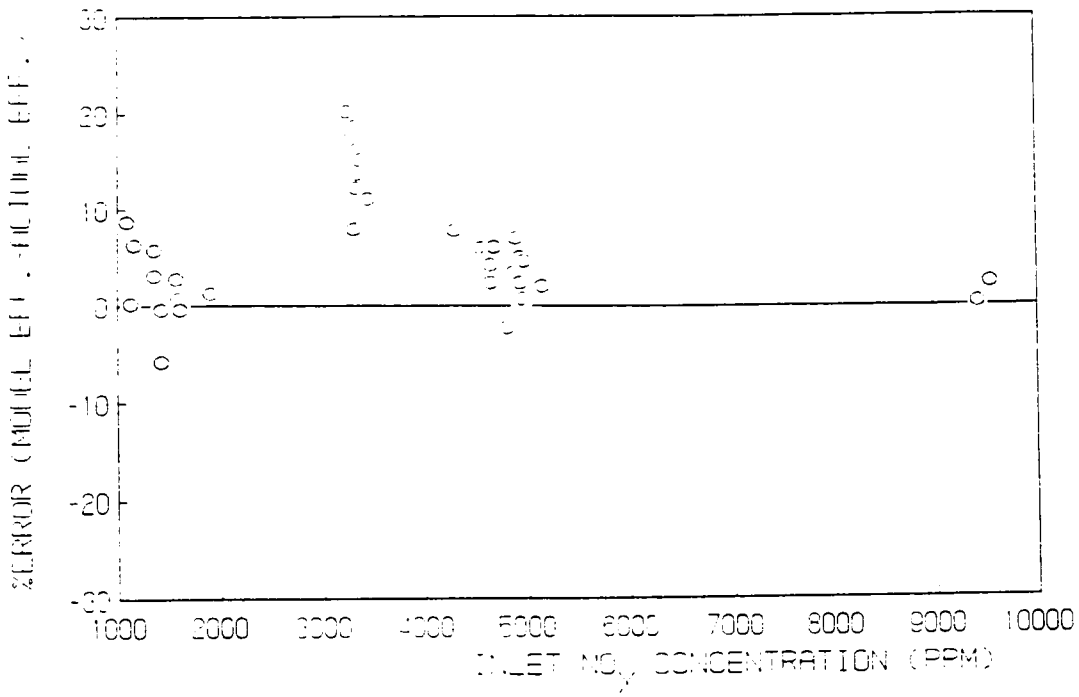


Figure 11. Residuals versus Inlet NO_x Concentration for Model 1 with Literature Parameters

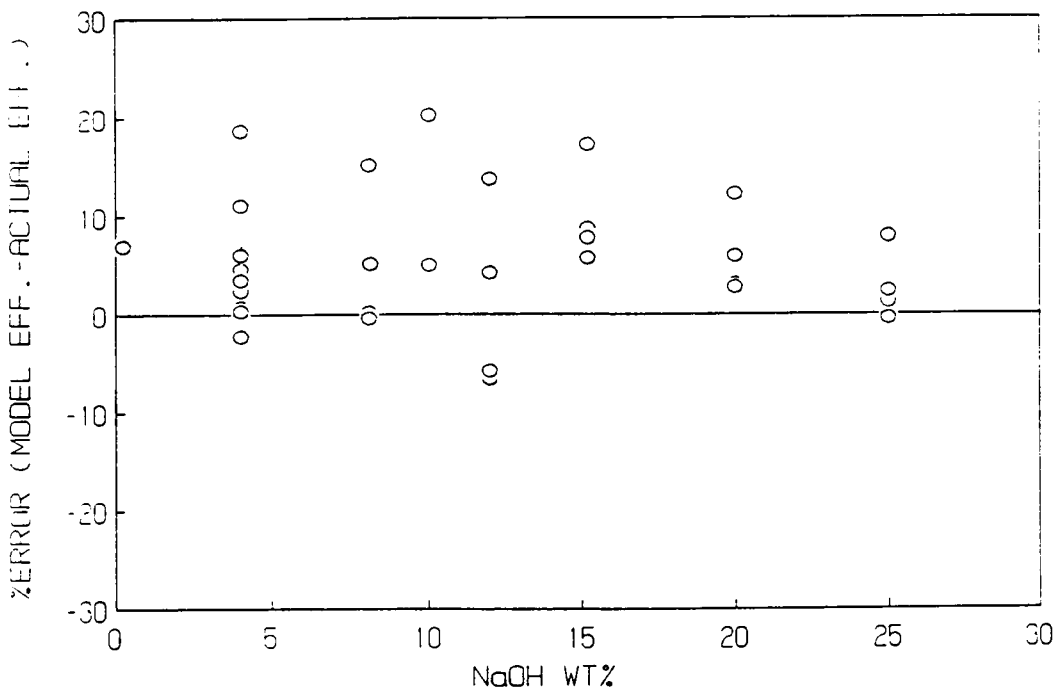


Figure 12. Residuals versus Hydroxide Wt. %
for Model 1 with Literature Parameters

NO_x removal efficiency. It was then discarded although only for the model input parameters used.

Model 1 was also used to predict absorption efficiencies using the optimized parameters. The average value of .126 was used for $(\sqrt{Dk}/H)_{N_2O_3}$. A line was regressed through the points on Figure 5 to obtain the optimized values for $(\sqrt{Dk}/H)_{N_2O_4}$.

$$(\sqrt{Dk}/H)_{N_2O_4} = 7.8 \times 10^{-4} - 1.365 \times 10^{-5} \times \text{WT. \% NaOH}$$

Figure 13 shows the effect of NO to NO_x ratio on the residuals using these parameters. The effect of inlet concentration is shown in Figure 14 and the effect of NaOH concentration in Figure 15. These figures show an improvement in the model predictions over the literature parameters. Figure 16 shows the model predictions compared to experimental data. The model agrees well with the data except for low NO to NO_x ratios, where it tended to overpredict efficiencies.

A few experimental data points were run using Koch/Sulzer packing and 5/8" flexirings. The model predictions for these runs are shown in Figure 17 and Figure 18, respectively. The parameters used for these predictions were those optimized from the Ceramic Intalox Saddles data.

As a comparison, this work supports the conclusions of Aoki et al. (1982), but not Carta (1984), or Newman and Carta (1988). Newman and Carta (1988) found that the formation and absorption of HNO_2 was a significant route. The model presented in this work was used to test Newman's data, but was generally unsuccessful, but it was noted that

the NO_x concentrations in his work were two to three orders of magnitude higher than the data used for this work.

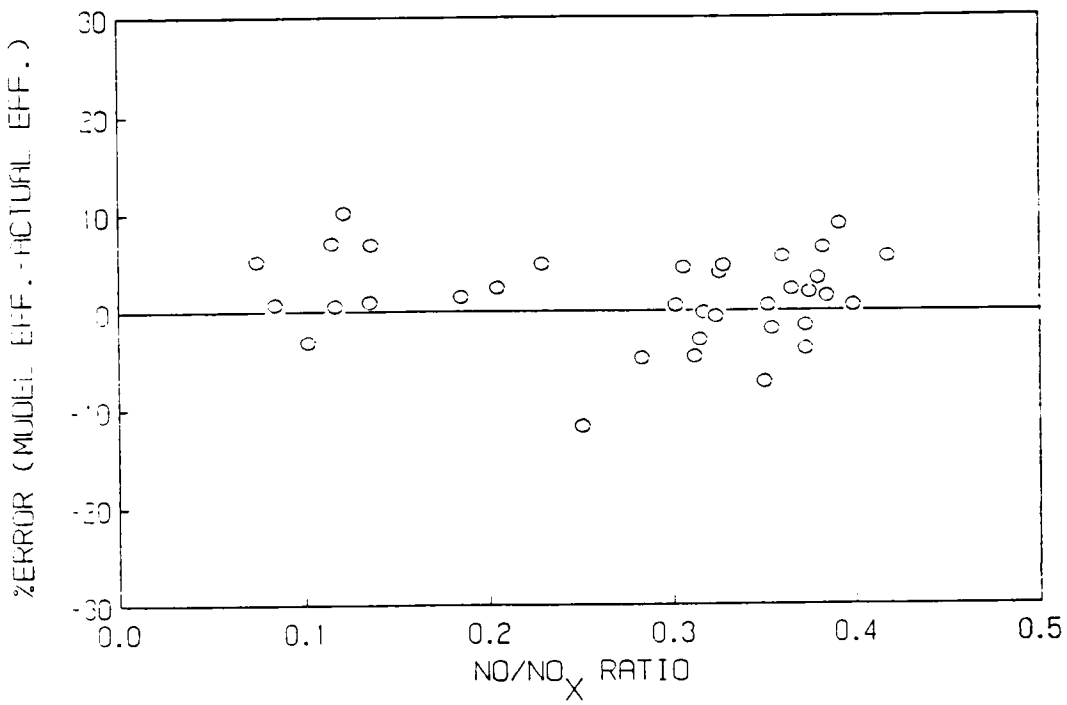


Figure 13. Residuals at Varying NO to NO_x Ratios for Model 1 Using Optimized Parameters

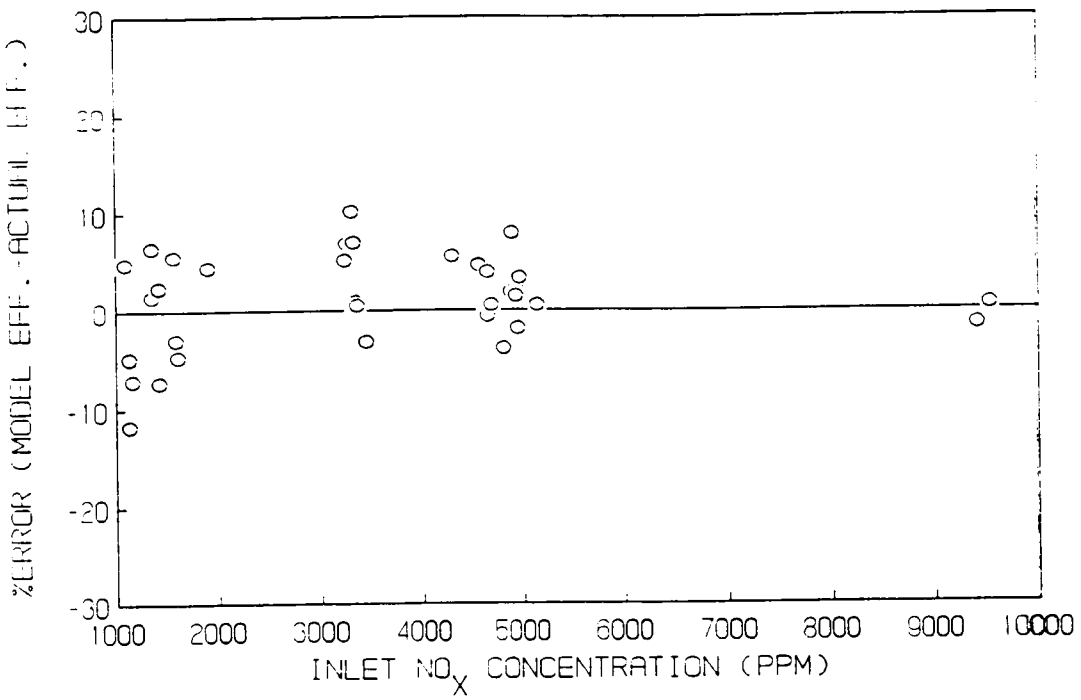


Figure 14. Residuals Versus Inlet NO_x Concentration for Model 1 Using Optimized Parameters

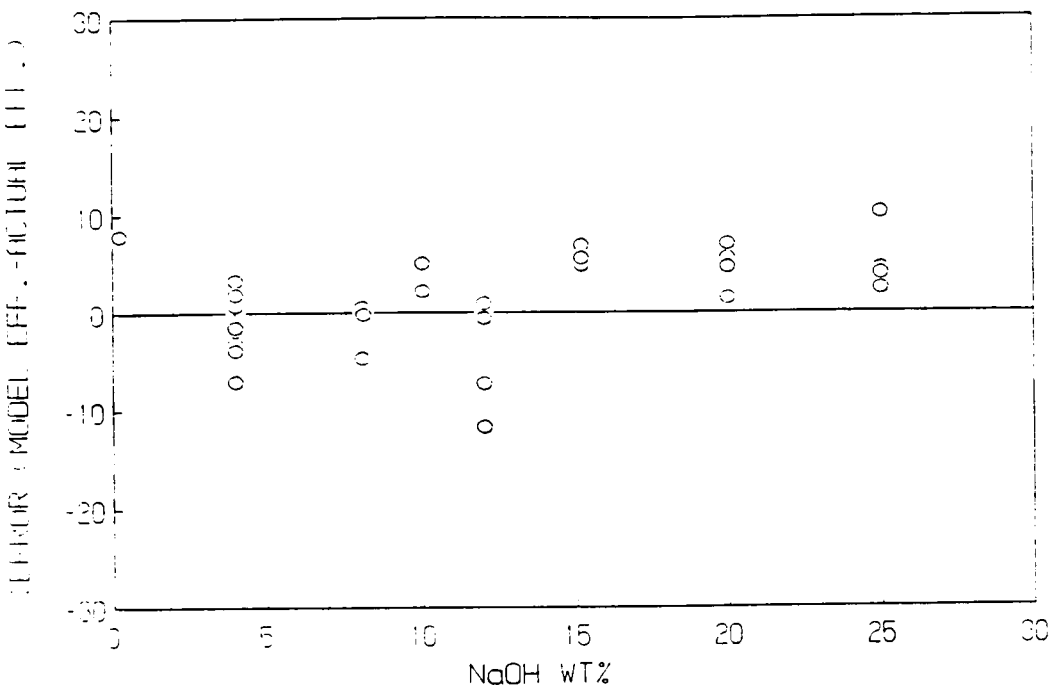


Figure 15. Residuals at Varying NaOH Concentrations for Model 1 Using Optimized Parameters

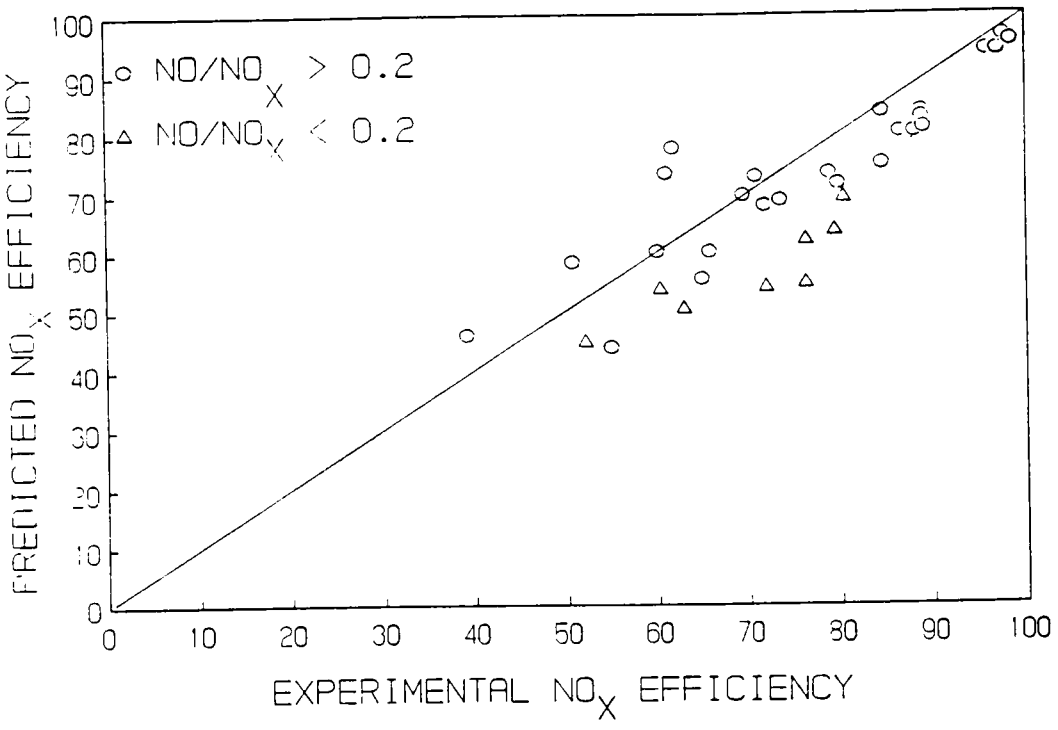


Figure 16. Model Comparison to Data for Ceramic Intalox Saddles Using Optimized Parameters for Model 1

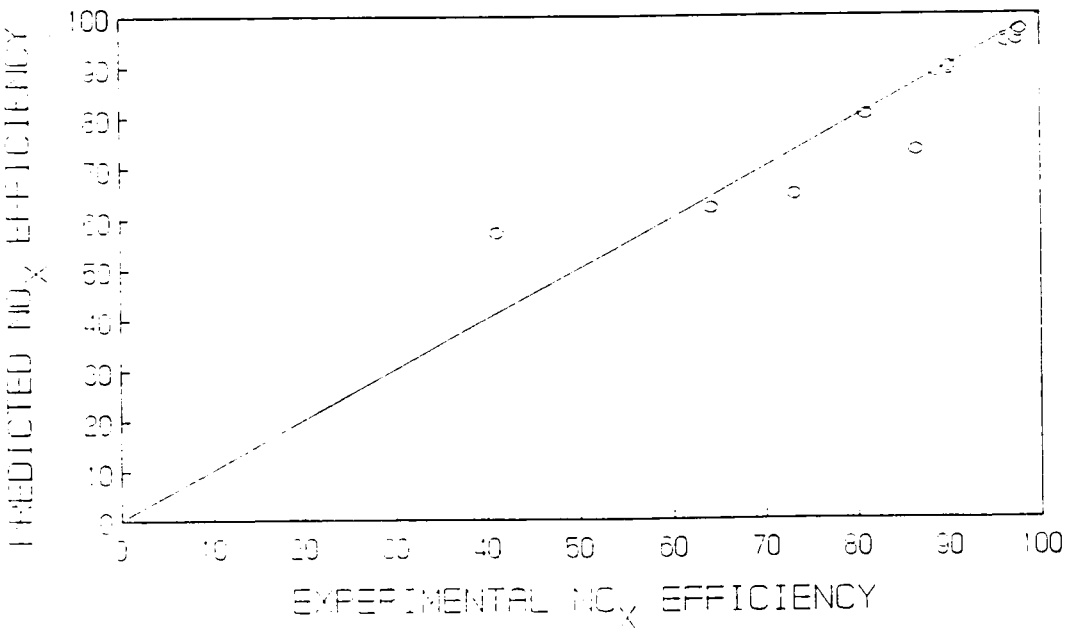


Figure 17. Model Comparison to Data for Koch/Sulzer Packing Using Optimized Parameters for Model 1

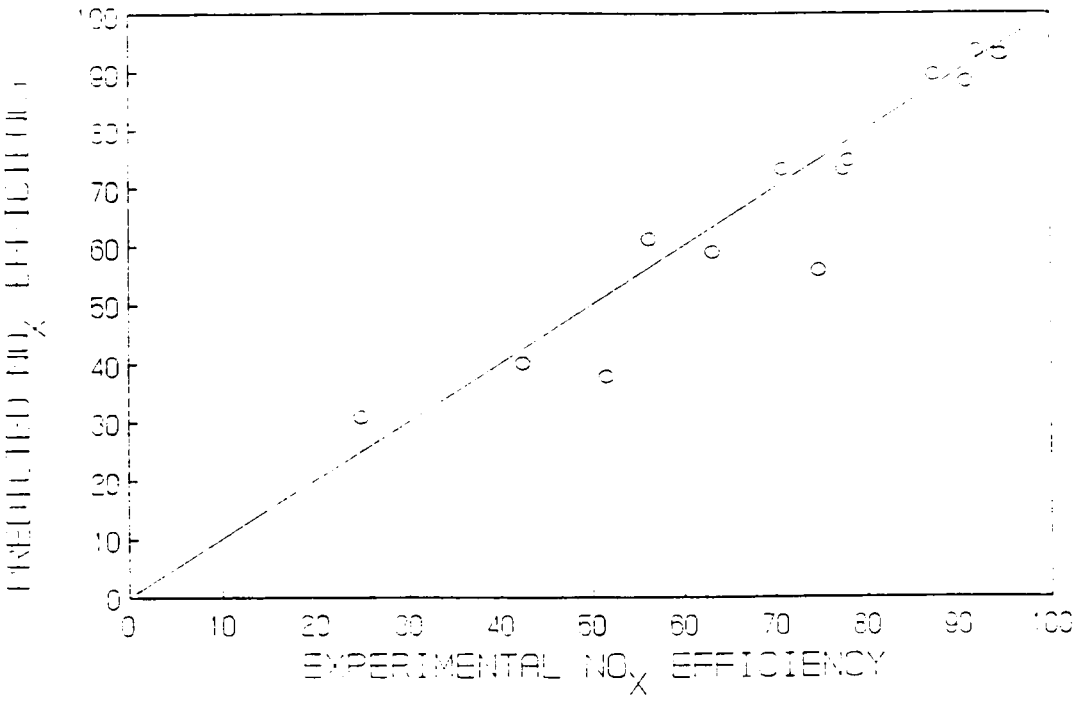


Figure 18. Model Comparison to Data for Flexirings
Using Optimized Parameters for Model 1

CONCLUSIONS

1. The absorption of NO_x from NO^* - NO_2^* mixtures into caustic solutions was observed to increase with the ratio of NO^* to NO_2^*, an effect opposite to the absorption into water.

2. An average value for $(\sqrt{Dk}/H)_{N_2O_3}$ of 0.126 agrees with 0.10 $kmol/m^2$ atm sec reported by Aoki et al.

3. Models providing for N_2O_4 and N_2O_3 absorption described most of the data reasonably well.

4. All efforts to model this sytem are highly dependent on input parameters. Due to uncertainty of k_G and other model input parameters, other models, possibly including HNO_2 absorption, cannot completely be ruled out.

RECOMMENDATIONS

1. Future experimental work should be conducted so that uncertainty in model input parameters can be reduced or eliminated. For example, mass-transfer coefficients can be more accurately estimated by first running experiments with CO_2 absorption.

2. The mechanisms of absorption in this system should be studied on other equipment such as a flat surface absorber.

3. A wider range of NO^*/NO_2^* ratios should be studied, including excess of NO^*.

4. The possibility of the formation and absorption of HNO_2 should be further studied.

5. The effect of the ionic strength of the Henry's law constants could be further defined.

6. The diffusivities of the individual NO_x specie in NaOH solutions should be studied.

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APPENDICES

APPENDIX A

Model Predictions

Run	NO Efficiency		NO_2 Efficiency		NO_x Efficiency		
	Model	Actual	Model	Actual	Model	Actual	NO/NO_x
1	62.1	78.6	33.4	38.1	39.2	46.3	.204
2	63.1	90.3	44.8	44.7	50.6	58.6	.305
3	88.5	83.3	47.0	39.7	52.1	44.9	.121
4	83.8	92.7	64.4	63.5	70.8	73.1	.325
5	77.8	72.1	55.2	60.7	60.9	73.6	.250
6	76.1	72.1	65.7	68.8	69.3	69.9	.350
7	97.6	62.2	73.0	62.3	76.3	62.3	.135
8	94.9	92.0	82.5	74.8	86.5	80.4	.323
9	98.2	41.7	74.5	55.9	76.2	54.8	.074
10	93.3	89.4	86.6	76.4	89.0	81.1	.364
11	87.5	87.3	89.4	81.8	88.7	83.9	.384
12	78.9	72.3	80.3	71.4	79.8	71.8	.379
13	97.5	98.8	96.9	91.4	97.1	94.1	.366
14	99.4	99.2	97.7	93.5	98.3	95.5	.352
15	43.4	72.8	73.4	81.5	61.7	78.1	.391
16	76.8	76.3	61.1	54.3	65.6	60.5	.283
17	82.1	80.0	69.5	64.0	73.4	68.9	.311
18	97.8	56.4	76.9	64.9	79.3	63.9	.116
19	74.8	74.4	42.1	40.0	48.2	46.4	.185
20	61.4	67.7	58.9	54.9	59.9	60.3	.417
21	95.0	75.3	58.8	47.3	62.9	50.5	.114

	NO Efficiency		NO_2 Efficiency		NO_x Efficiency		
Run	Model	Actual	Model	Actual	Model	Actual	NO/NO_x
22	90.3	93.8	73.2	63.7	78.8	73.6	.327
23	75.0	80.0	48.7	33.3	54.8	44.0	.229
24	69.0	73.1	62.3	45.2	64.9	55.9	.382
25	96.8	82.9	67.8	49.6	71.8	54.2	.136
26	91.1	93.7	80.6	64.7	84.4	75.1	.359
27	95.0	91.8	84.8	75.3	88.0	80.5	.316
28	80.8	72.9	57.5	51.4	60.3	54.0	.120
29	76.1	84.8	69.7	60.6	71.7	68.2	.314
30	96.0	71.4	78.6	69.0	80.4	69.3	.101
31	92.4	92.2	85.6	75.2	87.7	80.3	.302
32	84.3	87.2	84.7	82.1	84.5	84.0	.372
33	96.8	98.7	95.2	91.5	95.8	94.1	.354
34	98.2	99.3	97.5	95.0	97.7	96.6	.372
35	96.1	67.9	77.9	63.5	79.4	63.9	.084
36	88.3	89.0	88.8	79.3	88.6	83.0	.374

Run	$(\sqrt{Dk}/H)_{N_2O_3}$	$(\sqrt{Dk}/H)_{N_2O_4}$
1	.087	4.2×10^{-4}
2	.12	1.12×10^{-4}
3	.04	2.64×10^{-4}
4	.069	2.58×10^{-4}
5	.119	1.75×10^{-3}
6	.119	1.58×10^{-3}
7	.027	7.57×10^{-4}
8	.077	5.74×10^{-4}
9	.0134	6.4×10^{-4}
10	.070	4.94×10^{-4}
11	.074	6.8×10^{-4}
12	.076	9.41×10^{-4}
13	.047	3.26×10^{-4}
14	.030	2.37×10^{-4}
15	.047	8.7×10^{-4}
16	.131	1.05×10^{-3}
17	.119	1.09×10^{-3}
18	.023	8.59×10^{-4}
19	.08	5.74×10^{-4}
20	.091	2.58×10^{-4}
21	.033	3.94×10^{-4}
22	.075	2.53×10^{-4}
23	.118	2.81×10^{-4}

Run	$(\sqrt{Dk}/H)_{N_2O_3}$	$(\sqrt{Dk}/H)_{N_2O_4}$
24	.106	---
25	.045	4.21×10^{-4}
26	.084	1.96×10^{-4}
27	.076	6.16×10^{-4}
28	.091	1.34×10^{-3}
29	.136	7.95×10^{-4}
30	.035	9.68×10^{-4}
31	.075	6.38×10^{-4}
32	.104	1.08×10^{-3}
33	.067	5.17×10^{-3}
34	.049	3.78×10^{-4}
35	.030	8.06×10^{-4}
36	.075	5.86×10^{-4}

APPENDIX B

```
      IMPLICIT REAL*8(A-H,L-Z)
           COMMON GIN,LIN,OHC,NOIN,NO2IN,NOOUT,NO2OUT
           INTEGER Q
           REAL*8 K1,K2,K3,KK,KKP,KKNP,KKPP,KKKNP,KKKPP
C          HYDROXIDE SCRUBBER MODEL
C          1987  ANDREW LUCERO
C          UNIVERSITY OF TENNESSEE
C           KNOXVILLE,TENNESSEE
           k1=10.5620
        k2=1.87
           k3=0.7020
C  D IS THE DIFFUSIVITY
C
           dn2o4=9.3780d-06
           dn2o3=1.1075d-05
           dhno2=1.08914d-05
        dno2=1.3078d-05
           DNO=2.19*DHNO2
           HIN2O3=2.59*.72/.769
           HIN2O4=0.72
           HINO2=142.7
           hihno2=1./60.
C NOTE THESE CONSTANTS FOR ATM NOT PASCAL
C
C KK=RATE CONSTANT FOR RXN N2O4 W/H2O --KKP FOR RXN W/OH
           KK=250
           WRITE(*,*)'KL FACTOR kn2o3   STEP'
           READ(*,*)ZZZ,zz2,STEP
                ITEP=STEP
           WRITE(6,*)'KL FACTOR kn2o3',zzz,zz2
        KKP=147*17./40.
           RHOAIR=1.185
           MUAIR=1.80D-05
           MUH2O=.1/100.
            AP=623
C EPS=VOID FRACTION
             EPS=0.78
           DP=.0165
           F=2.03
               L=.25*.013
           DCOL=4.25*2.54/100
           CSA=DCOL**2*3.1415926/4
           DZ=HCOL/50.
 23        FORMAT(I2)
 28        FORMAT(D7.1)
            READ(9,*)ICASE
            DO 91 I=1,ICASE
           IPASS=IPASS+1
            read(9,*)gin,lin,ohc,noin,NO2IN,NOOUT,NO2OUT
c          WRITE(6,*)gin,lin,ohc,noin,NO2IN,NOOUT,NO2OUT
```

```
      IF(OHC.LT.0.05)THEN
           READ(9,*)HCOL
      ELSE
      HCOL=33.*2.54/100
      END IF
       WRITE(7,66)
66       FORMAT(2X,'Gin',10X,'Lin',10X,'OHC')
22    format(4X,'NOIN',15X,'NO2IN',15X,'NOOUT',15X,'NO2OUT')
        WRITE(7,67)gin,lin,ohc
        WRITE(7,22)
        WRITE(7,16)NOIN,NO2IN,NOOUT,NO2OUT
67      FORMAT(1X,F5.2,8X,F5.2,12X,F5.2)
16      FORMAT(F10.2,10X,F10.2,10X,F10.2,10X,F10.2)
        WRITE(7,*)' '
        WRITE(7,*)' '
        IF(OHC.LT.0.05)GOTO 333
        G=GIN/60*0.028317
        L=LIN/60*0.028317/7.48
         PNO2IN=NO2IN*1D-06
         PNOIN=NOIN*1D-06
         PNOOUT=NOOUT*1D-06
         PNO2OUT=NO2OUT*1D-06
333     CONTINUE
         RHOL=1000*(1+.0111*OHC)
        WRITE(7,*)' '
         VG=G/CSA
         VL=L/CSA
         RNOX=PNOIN/(PNO2in+PNOIN)
         WRITE(6,*)'NO/NOX IN',RNOX
         PNOOUT=NOOUT*1D-06
         PNO2OUT=NO2OUT*1D-06
        PNO2S=(PNO2IN-PNO2OUT)/DLOG(PNO2IN/PNO2OUT)
        PNOS=(PNOIN-PNOOUT)/DLOG(PNOIN/PNOOUT)
        ANOX=PNOS/(PNOS+PNO2S)
        WRITE(6,*)'NO/NOX AVE',ANOX
        WRITE(6,*)' '
        WRITE(6,*)' '
      WRITE(6,*)'PNO2*,PNO*AVERAGE',PNO2S*101325,PNOS*101325
      WRITE(6,*)' '
      WRITE(6,*)' '
        PNO=PNOS
        PNO2=PNO2S
         IF (OHC.EQ.0.0 .OR. OHC.EQ.0.25)PW=17.5/760.0
         IF (OHC.EQ.0.0.OR.OHC.EQ.0.25)MUL=.1/100.
         IF (OHC.EQ.4.0)PW=17.02/760.0
         IF (OHC.EQ.4.0)MUL=.1246/100.
         IF (OHC.EQ.8.1)PW=16.36/760.0
         IF (OHC.EQ.8.1)MUL=.1613/100.
      IF (OHC.EQ.12.0)PW=15.58/760.0
      IF (OHC.EQ.12.0)MUL=.2197/100.
```

```
        IF (OHC.EQ.2.0)MUL=.1141/100.
        IF (OHC.EQ.5.0)MUL=.1326/100.
        IF (OHC.EQ.14.)MUL=.2563/100.
        IF (OHC.EQ.6.0)MUL=.1413/100.
        IF (OHC.EQ.1.0)MUL=.1052/100.
        IF (OHC.EQ.1.0)pw=17.38/760
        IF (OHC.EQ.2.0)pw=17.26/760
        IF (OHC.EQ.6.25)pw=16.72/760
        IF (OHC.EQ.8.33)pw=16.36/760
        IF (OHC.EQ.3.0)MUL=.1174/100.
        IF (OHC.EQ.9.0)MUL=.1734/100.
        IF (OHC.EQ.8.0)MUL=.1613/100.
        IF (OHC.EQ.7.0)MUL=.1507/100.
        IF (OHC.gt.15.1.and.ohc.lt.15.3)PW=14.95/760.0
        IF (OHC.lt.15.3.and.ohc.gt.15.1)MUL=.2783/100.
        IF (OHC.EQ.20.0)PW=13.90/760.0
        IF (OHC.EQ.20.0)MUL=.4610/100.
        IF (OHC.EQ.25.0)PW=12.60/760.0
        IF (OHC.EQ.25.0)MUL=.79065/100.
          WRITE(6,*)'MUL',MUL
           RT=2.4202d6
           write(*,*)'ohc',ohc
           ohc=ohc/.040*rhol/100000
C TOTAL PRESSURE IS 1ATM
C
C ABOVE ARE UNIT CONVERSIONS
C IONIC STRENGTH AND HENRY'S LAW CONSTANTS PROBABLY
C
C
         NI=OHC
          ohc=ohc*.040/rhol*100000.
          HNO2=HINO2*10**(.157*NI)
C   THAT IS A HENRY'S LAW CONST
          HN2O4=HIN2O4*10**(.157*NI)
          HN2O3=HIN2O3*10**(.157*Ni)
          HhNo2=HIhno2*10**(.157*Ni)
c             WRITE(7,*)HN2O4,HIN2O4
c         write(*,*)GIN,LIN,OHC,NOIN,NO2IN,NOOUT,NO2OUT,'yyyy'
C PRESSURE STILL IN ATM
C
          B=101325.
          Y=K1/B*2
          Z=K3/B
          KK=194/55.70*(100.-OHC)*RHOL/.018/100000.
          DK=1.2D4/55.70*(100.-OHC)*RHOL/.018/100000.
         IF(DK.GT.1.2D4)DK=1.2D4
         IF(KK.GT.194.0)KK=194.
           WRITE(*,*)'KK,DK,',KK,DK
         THEP=(1.0D-9*MUH2O/MUL*(DK))**(.5)/(HN2O3)*7.7/5.8
         THEO=(1.23d-09*MUH2O/MUL*(KK+KKP*OHC*RHOL/100))**(.5)/(HN2O4)
```

```
                VV=CSA*HCOL
        PP=PNOS
        PP2=PNO2S
        PNOS=PNOIN
        PNO2S=PNO2IN
          DO 10 IIOU=1,12
           IF(PNO2.LE.0.0)PNO2=1D-08
           IF(PNO.LE.0.0)PNO=1D-08
           PHNO2=(K2*PNO2*PW*PNO)**.5
           PN2O4=K1*PNO2**2
           PN2O3=K3*PNO2*PNO
           PNO=PNOS-PN2O3-.5*phno2
           PNO2=PNO2S-2*PN2O4-PN2O3-.5*phno2
           IF(PNO.LE.0.0)PNO=1D-08
           IF(PNO2.LE.0.0)PNO2=1D-08
 10       continue
           pnos=pno+pn2o3+.5*phno2
                  PNO2S=PNO2+2*PN2O4+PN2O3+.5*phno2
C
         Write(6,*)'PNO2,NO,HNO2,N2O4,N2O3',PNO2,PNO,PHNO2,PN2O4,PN2O3
c interfacial area
           DNOS=(DNO*pno+dHno2*phno2/2+dhn2o3*pn2o3)/pnos
         DNO2S=(DNO2*pno2+DN2O4*pn2o4*2+DN2O3*pn2o3+DHNO2*phno2/2)/pno2s
           a=19.6*v1**(0.478)*.013**(-1.0)/EPS**3
           SCHNO2=MUAIR/(RHOAIR*DHNO2)
                  SCNOS=MUAIR/(RHOAIR*DNOS)
           SCNO2S=MUAIR/(RHOAIR*DNO2S)
C        EPSL=(1.53D-04+2.9D-05*(DCOL*VL*RHOL/MUL)**0.66
C     &   *(MUL/MUH2O)**0.75)*.013**(-1.2)
           NRE=.013*VL*RHOL/MUL
           GALLIL=.013**3*9.81*RHOL**2/MUL**2
           AD=.013*623.
           HOP=1.295*NRE**.676/GALLIL**.44*AD
           HSTAT=0.0317
           EPSL=HOP+HSTAT
           PM=F*623.*VG**3./(6.*(EPS-EPSL)**4.)
           P1=1-PNO-PNO2-PN2O4-PN2O3-PHNO2
           RT=2.4202D6
           WW=((PM*L)**(1./3.)*L*RHOAIR/MUAIR)**0.62*.553*1/P1
         GKGHNO2=WW*SCHNO2**(1./3.)*DHNO2/(L*RT)
         GKGNOS=WW*SCNOS**(1./3.)*DNOS/(L*RT)
         GKGNO2S=WW*SCNO2S**(1./3.)*DNO2S/(L*RT)
          SCLI=MUL/RHOL/2.D-09/MUH2O*MUL
          GCLI=MUL/RHOL/1.23D-09*ZZZ
         WL=VL*RHOL
       GKL=2.D-09*MUH2O/MUL*25.1*(DP*WL/MUL)**.45*SCLI**.5/DP
C       GKL=6.2D-05*(MUH2O/MUL)**.65
C CONVERT TO PASCAL HERE
         PNOS=PP*B
         PNO2S=PP2*B
```

```
      NNO2S=(PNO2IN-PNO2OUT)*B/A/HCOL/RT*VG
      NNOS=(PNOIN-PNOOUT)*B/A/HCOL/RT*VG
       WRITE(6,*)'NNO2S,NNOS',NNO2S,NNOS
       WRITE(6,*)'PNO2S,PNOS',PNO2S,PNOS
      PNOSI=PNOS-NNOS/GKGNOS
      PNO2SI=PNO2S-NNO2S/GKGNO2S
      WRITE(6,*)'PNO2*I,PNO*IAVERAGE',PNO2SI,PNOSI
        FF=(K3*PNO2SI*PNOSI)
        FX=(K1*PNO2SI**2)
        OTF=(K3*PNO2OUT*PNOOUT)
        OTX=(K1*PNO2OUT**2)
C
        E=1.+OHC*RHOL/100*hN2O3/FF/40.
        EOUT=1.+OHC*RHOL/100*hN2O3/OTF/40.
        E4OUT=1.+OHC*RHOL/100*hN2O4/OTX/40.
        EO4=1.+OHC*RHOL/100*hN2O4/FX/40.
     OHCOUT=OHC*RHOL/100*VL/40-(2*NNOS+2*(NNO2S-GKL/HNO2*PNO2*0))
      OHCOUT=OHCOUT/RHOL*100/VL*40
      WRITE(16,*)'OH CONC OUT     IN',OHCOUT,OHC
     WRITE(*,*)'E',E
      NEWTHEP=(NNOS)/(PNOSI*PNO2SI)
      HEO=(NNO2S-NNOS-GKL/HNO2/B*PNO2SI*0)/PNO2SI**2
       HEO=HEO/Y*B
       NEWTHEP=NEWTHEP/Z*B
       WRITE(16,*)'COMPARE E*KL>DK>3*KL',E*GKL,NEWTHEP*HN2O3,3*GKL
       WRITE(16,*)'COMPAREN2O4 E*KL>DK>3*KL',EO4*GKL,HEO*HN2O4,3*GKL
       WRITE(16,*)'NOTE ALSO RAN THESE FOR INLET AND EXIT'
       WRITE(16,*)'CONCENTRATIONS'
       WRITE(16,*)'  '
     write (16,*)'compARE M>10*E',NEWTHEP*HN2O3/GKL,10.*E
     write (16,*)'compARE N2O4 M>10*E',HEO*HN2O4/GKL,10.*EO4
       WRITE(16,*)'  '
      WRITE(23,*)'CALCULATED SQRT(DK/H*K)'
      WRITE(23,*)'N2O4          N2O3         OHC       NO/NOXin'
      WRITE(23,71)HEO,NEWTHEP,OHC,RNOX
71    FORMAT(5X,D9.3,5X,D9.3,5X,F5.2,5X,F7.3)
      WRITE(6,*)' '
      WRITE(6,*)' '
      WRITE(6,*)'CALCULATED SQRT(DK/H*K)'
      WRITE(6,*)'NO2           NO        OH- , CONC.'
      WRITE(6,*)HEO,NEWTHEP,OHC
       WRITE(6,*)'KGNO2,KGNO,KL',GKGNO2S,GKGNOS,GKL
     WRITE(6,*)'DK/H CALC   THEORETICALN2O4'
     WRITE(6,*)HEO,THEO
     WRITE(6,*)'DK/H CALC  THEORETICAL N2O3'
     WRITE(6,*)NEWTHEP,THEP
      WRITE(6,*)' '
      WRITE(6,*)' '
      R11=HEO/THEO
      R22=NEWTHEP/THEP
```

```
      WRITE(6,*)'RATIO N2O4,N2O3',R11,R22
       MNO4=(HEO*HN2O4)**2/GKL**2
       MNO3=(NEWTHEP*HN2O3)**2/GKL**2
       WRITE(6,*)'FILM CONVERSION PARAMETERS'
       WRITE(6,*)'N2O4,N2O3',MNO4,MNO3
       WRITE(6,*)' '
       WRITE(6,*)' '
        ndd=2d-9
        npp=1.23d-09
      KKNP=(NEWTHEP**2*HN2O3**2/ndd-DK)/OHC/RHOL*100
      KKPP=(HEO*HEO*HN2O4**2/npp-KK)/OHC/RHOL*100
     kkknp=kknp/ohc/rho1*100
     kkkPp=kkPp/ohc/rho1*100
      IF(ANOX.GT.0.18)THEN
        suds=suds+kkknp
           SUM=SUM+KKNP
         SUN=SUN+KKPP
         SS=SS+1
         ANOX=0.
      END IF
        WRITE(6,*)'KN2O3 W/OH',KKNP,kkknp
     bedo=(2D-9*(kknp+kkpp)*ohc*rho1/100)**.5
     dedo=gk1*(1+ohc*rho1/100./40./(2*pn2o3/hn2o3+pn2o4/hn2o4*2))
        write(6,*)'KPRIME CALCULATED'
        write(6,7)
7     format(2X,'n2o4',10x,'n2o3',12x,'n2o3(oh^2)',4x,'ohc')
        write(6,3)KKPP,KKNP,KKKNP,OHC,KKKPP
3    FORMAT(F9.3,5X,D9.3,5X,D9.3,5X,F7.3,9x,f7.3)
5    FORMAT(E8.3)
97     CONTINUE
       WRITE(7,*)' '
        write(*,*)gin,lin,ohc,pnos,pno2s,pnoout,pno2out
        write(*,*)gkgno2s,gkgnos
      BBB=OHC*RHOL*zz2/100+DK
      AAA=OHC*RHOL*147.0/100+KK
      THEP=(2D-9*BBB)**.8/HN2O3*Z/B
      THEO=(1.23D-09*AAA)**.5/HN2O4*Y/b
C     THEO=HEO*Y/B
C     THEP=NEWTHEP*Z/B
        WRITE(7,*)'THEO THEP',THEO,THEP
        DZ=HCOL/STEP
        PNO2S=PNO2IN
        PNOS=PNOIN
        DO 88 J=1,ITEP
              DO 15 JP=1,20
        IF(PNO.LT.0.0)THEP=0
        IF(PNO2.LT.0.0)THEO=0
        IF(PNO.LT.0.0)PNO=1D-9
        IF(PNO2.LT.0.0)PNO2=1D-9
         PHNO2=(K2*PNO2*PW*PNO)**.5
```

```
            PN2O4=K1*PNO2**2
            PN2O3=K3*PNO2*PNO
            PNO=PNOS-PN2O3-.5*phno2
            PNO2=PNO2S-2*PN2O4-PN2O3-.5*phno2
           IF(PNO.LT.0.0)PNO=1D-9
           IF(PNO2.LT.0.0)PNO2=1D-9
 15        CONTINUE
            pnos=pno+pn2o3+.5*phno2
                    PNO2S=PNO2+2*PN2O4+PN2O3+.5*phno2
           PNOS=PNOS*B
           PNO2S=PNO2S*B
 37        A1=THEO*PNO2S**2
           A2=-2*THEO*PNO2S*NNO2S/GKGNO2S
           A3=THEO*NNO2S*NNO2S/GKGNO2S**2
           Z1=THEP*(PNO2S-NNO2S/GKGNO2S)
           A4=PNOS*Z1*GKGNOS/(GKGNOS+Z1)
           A5=GKL/HNO2/B*(PNO2S-NNO2S/GKGNO2S)
           A6=0.
           A7=-NNO2S
           FN=A1+A2+A3+A4+A5+A6+A7
           AP1=0.
           AP2=-2*THEO*PNO2S/GKGNO2S
           AP3=2*THEO*NNO2S/GKGNO2S**2
           AP4=(GKGNOS+Z1)*(-PNOS*THEP*GKGNOS/GKGNO2S)
           AP5=PNOS*Z1*GKGNOS*THEP/GKGNO2S
           AP6=(AP4+AP5)/(GKGNOS+Z1)**2
           AP7=GKL/HNO2/B*(-1/GKGNO2S)
           AP8=-1.
           FP=AP1+AP2+AP3+AP6+AP7+AP8
           NN=NNO2S-FN/FP
           TEST=ABS((NN-NNO2S)/NNO2S)
           JJ=JJ+1
           NNO2S=NN
           IF(TEST.GT.1D-8.AND.JJ.LE.1000)GOTO37
           NNOS=(PNOS*GKGNOS*Z1)/(GKGNOS+Z1)
 31          CONTINUE
 89        CONTINUE
C
            PNO2S=PNO2S-NNO2S*A*DZ*RT/VG
            PNOS=PNOS-NNOS*A*DZ*RT/VG
           PNOS=PNOS/B
           PNO2S=PNO2S/B
 88        CONTINUE
           XEFNOX=(1.-(PNO2S+PNOS)/(PNO2IN+PNOIN))*100.
           DEFNOX=(1.-(PNOOUT+PNO2OUT)/(PNO2IN+PNOIN))*100.
           WRITE(7,*)'NOX EFFICIENCY'
           WRITE(7,*)'MODEL            ACTUAL       NO/NOXIN'
           WRITE(7,9)XEFNOX,DEFNOX,RNOX
           MEFNO=(1.-PNOS/PNOIN)*100.
           MEFNO2=(1.-PNO2S/PNO2IN)*100.
```

```
      REFNO2=(1.-PNO2OUT/PNO2IN)*100.
      REFNO=(1.-PNOOUT/PNOIN)*100.
      WRITE(7,*)'NO* EFFICIENCY'
      WRITE(7,*)'MODEL                ACTUAL              NO/NOXIN'
      WRITE(7,9)MEFNO,REFNO,RNOX
      WRITE(7,*)'NO2* EFFICIENCY'
      WRITE(7,*)'MODEL                ACTUAL              NO/NOXIN'
      WRITE(7,9)MEFNO2,REFNO2,RNOX
 9    FORMAT(F9.3,12X,F9.3,12X,F9.3)
      WRITE(6,*)' '
      WRITE(7,*)' '
      WRITE(7,*)' '
91     CONTINUE
       AVERAG=SUN/SS
      WRITE(7,*)' '
      WRITE(7,*)' '
      WRITE(7,*)'AVE KN2O4',AVERAG
         AVER=SUM/SS
         AVss=SUds/ss
         WRITE(7,*)'AVERAGE KKKNP',AVER
         WRITE(7,*)'AVERAGE KKKNPwith oh^2',AVss
      STOP
      END
```

APPENDIX C

IDEAL GAS ASSUMPTION CHECK FOR NO_2

IDEAL GAS LAW

$P * V = R * T$

$V = R * T/P$

$= 0.7302$ atm-ft^3/lbmol-R * 524.4 R/1.0 atm

$= 382.9$ ft^3/lbmol

van der Waals EQUATION

$(P + a/VS)(V - b) = R * T$

$a = 27/64 * R^2 * Tc^2/Pc$

$= 1356.35$

$= R * TC/(8 * Pc)$

$= .7088$

$V = 380.1$ ft^3/lbol

Percent Error of IDEAL GAS LAW

$=$ ABS(382.9-380.1)/380.1 * 100

$= 0.7\%$

VITA

Andrew J. Lucero was born in Espanola, New Mexico. He attended high school in Johnson City, Tennessee. He graduated from University High School in June 1980. He attended college at The University of Tennessee, Knoxville, and received a Bachelor of Science in Chemical Engineering.