To the Graduate Council:

I am submitting herewith a thesis written by Tracy J. Coates entitled "NOx Absorption from Air Streams Using Aqueous Sodium Hydroxide and Hydrogen Peroxide Solutions." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

R. M. Counce

R.M. Counce, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

CWMinkel

Vice Provost
and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at the University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under the rules of the Library. Brief quotations from this work are allowable without special permission, provided that accurate acknowledgment of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature ______________________

Date 14 Nov 86

NOx ABSORPTION FROM AIR STREAMS USING AQUEOUS SODIUM HYDROXIDE AND HYDROGEN PEROXIDE SOLUTIONS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Tracy J. Coates
December 1986

ABSTRACT

Control of Nitrogen oxide (NOx) emissions is of increasing importance to and presents special problems for batch process sources. These sources typically generate varying amounts of NOx which in conjunction with a varying NO to NO_2 ratio causes the removal of NOx from these streams to be complicated.

Models for NOx absorption into water, aqueous Sodium hydroxide and aqueous Hydrogen peroxide were developed for evaluation for a optimal absorption solution. The Sodium hydroxide and Hydrogen peroxide models both showed an improvement over the use of water for the absorption media. Comparison of the results from the models indicate that the Sodium Hydroxide solution would be preferred for NOx levels above $5 * 10^{-4}$ atm. Below this level the Hydrogen peroxide solution would be recommended. Results obtained from the model for NOx absorption into water were found to match well with experimental data.

TABLE OF CONTENTS

I. INTRODUCTION

There are a significant number of processes in the Chemical Process Industry (CPI) that generate Nitrogen oxides (NOx) as a gaseous emission to the atmosphere. These emissions have long been addressed under the Federal Clean Air Act which places limits on both the absolute discharge concentrations and the stack gas opacity which results from the presence of NOx. New amendments to the Clean Air Act are expected as result of increased concern over 'acid rain' that will further reduce the acceptable NOx discharge limits and create increased pressure on CPI operations to reduce these emissions.

Of the CPI processes that produce NOx emissions there are three of particular interest due to their batch operation;

1. steel pickling;
2. precious metal processing, specifically the recovery of these metals from substrates by leaching with Nitric acid solutions;
3. uranium processing, again specifically for the leaching of Uranium from substrates with Nitric acid solutions.

Interest in these processes results from two factors common to these processes that cause their emissions to be difficult to control to lower standards. The first of these factors is the cyclic nature of their batch operations. This characteristic results in a rapid increase in NOx levels to a peak early in the cycle and then decreasing through the cycle until completion. As the absorption of NOx is highly concentration dependent the relative removal of NOx per unit column height decreases with a decrease in the NOx partial pressure.

The second factor is that it has been shown that the oxidation state of NOx (NO vs. NO_2) is of importance in determining the NOx removal. This second factor occurs in these batch systems as result of varying Nitric acid concentrations in the process solutions. The formation of NO_2 is favored at higher acid concentrations and NO formation at lower concentrations (Harrington, 1959; Interel, 1982), therefore as the batch progresses a natural decrease in NO_2 in favor of NO will occur. This will then result in a decrease in the NOx removal efficiency as the chemical NO species are much less soluble in water than the chemical NO_2 species.

In this study the objective was to compare the relative efficiencies of three absorbers for gas streams of varying NOx levels and NO/NO_2 ratios. These absorbers were modeled at identical cross-sectional area, height, packing type and environmental conditions. Model A utilized water as the absorbing solution, Model B a 3%

Sodium hydroxide solution and Model C a 3% Hydrogen peroxide solution.

II. LITERATURE SURVEY

The absorption of NOx has been extensively studied in both theoretical and experimental studies. As such there is a large body of information available on the subject especially relating to the absorption of NOx by water (Counce, 1980). The purpose of this literature survey is to provide a summary of the literature relating to the three models that were developed for this study.

Water Absorption Model

This model is based on the absorption of N_2O_4 and N_2O_3 into the liquid phase and gas phase oxidation of NO to NO_2. The absorption of other NOx components is considered to be insignificant due to:

1. low solubility of NO and NO_2 (Counce,1980);
2. liquid phase inhibition to nitrous acid (HNO_2) absorption (Carta, 1984);
3. extremely low concentrations in the gas phase for nitric acid (HNO_3) (Carta, 1984).

Absorption of N_2O_4 and N_2O_3 has been shown (Counce, 1980) to occur with the following reactions;

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (1)$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad (2)$$

In both cases the absorption of N_2O_4 and N_2O_3 into water has been found to normally be liquid phase dependent in packed towers (Sherwood, Pigford, Wilke, 1974). The absorptive fluxes for these components may be defined as;

$$R_3 = (H\sqrt{D * k})_3 * P_3 \qquad (3)$$

$$R_4 = (H\sqrt{D * k})_4 * P_4 \qquad (4)$$

Included in their definition of these flux terms by Sherwood et al. (1974) is their independence of concentration effects in the liquid phase for dilute systems. This latter point from k being independent of concentration by definition and H being a constant at the low concentrations involved in this model. The last term, D, in the flux equation is also independent of concentration for dilute systems as shown by the Wilke-Chang estimation technique (Reed, et al., 1977).

Several values have been proposed for $H\sqrt{Dk}$ for N_2O_4 and N_2O_3 from which $8.8^4 * 10^{-4}$ was selected for N_2O_4 (Counce, 1980) and 0.00159 for N_2O_3 (Sherwood, et al., 1975), both in units of kmol/m^2-s-atm.

The oxidation of NO to NO_2 in the gas phase is an essentially irreversible reaction (5) for which the

$$NO + 1/2O_2 \longrightarrow NO_2 \qquad (5)$$

reaction rate constant was found by Boderstein (1922) to have a value of 23.49 $atm^{-1}s^{-1}$ at the evaluation temperature of 300 K.

The desorption of NO resulting from the decomposition of HNO_2 in the liquid phase was reviewed by Counce (1980) and was determined to be dependent upon;

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO \qquad (6)$$

This reaction from the work of Abel and Schmid (1929) was developed for absorption at near atmospheric pressure and NO^* partial pressures of less than 0.0123 atm. Though applicable to the current model examination of typical reaction rates for reaction (6) demonstrate that this desorption mechanism is insignificant.

Sodium Hydroxide Model

The model for absorption and reaction mechanisms into solutions of Sodium hydroxide (Model B) is the same as that developed for Model A above with the the addition of an HNO_2 absorption mechanism. This additional absorption path was proposed by Carta (1984) as a gas phase limited absorption with a flux equation of;

$$R_5 = k_{g5} * P_5 + \frac{D_5 * K}{2 * R * T * k_{g5}} * P_1 * P_2 * P_{12} \qquad (7)$$

Included in this equation is the assumption of instantaneous irreversible reaction of HNO_2 with NaOH at the interface. This is based upon the large NaOH concentration as compared to HNO_2 at the interface which classifies the reaction as a Case B in the nomenclature presented by Levenspiel (1972). This approach is simular to that proposed by Carta (1984) whose calculations of NOx absorption into alkaline solutions agreed well with industrial observations.

Calculation of the diffusion coefficient for HNO_2 may be accomplished for dilute aqueous solutions using a method presented by Sherwood et al. (1974);

$$D_5 = (14.0 * 10^{-5}) * V_5^{-0.6} * \mu_{12}^{-1.1} \qquad (8)$$

The gas phase mass transfer coefficient may also be calculated with the method proposed by Onda et al. (1968) being;

$$k_{g5} = 5.23 * \frac{a * D_5}{R * T} * \left(\frac{G}{a * \mu_g}\right)^{0.7} * \left(\frac{\mu_g}{g * D_5}\right)^{-0.33} * (a * D_p)^{-2} \qquad (9)$$

Hydrogen Peroxide Absorption Model

The first difference between this model (C) and Model A is the gas phase oxidation of NO_2 by H_2O_2 via the reactions;

$$NO_2 + H_2O_2 \longrightarrow HNO_3 + OH^- \qquad (10)$$

$$NO_2 + OH^- \longrightarrow HNO_3 \qquad (11)$$

This reaction sequence was proposed by Gray, et al. (1972) along with a reaction rate coefficient for the rate determining step, reaction (10), of 12.24 $atm^{-1}s^{-1}$. In the same study a gas phase reaction was proposed between NO and H_2O_2 but with a rate constant of 1.28 $atm^{-1}s^{-1}$. This reaction was considered insignificant to the model.

Another NO-H_2O_2 mechanism is proposed by Baveja, et al. (1979) to exist in the liquid phase. In this case the

$$R_l = S_l * \sqrt{D_l * k} * \sqrt{C_g} \qquad (12)$$

flux term (equation 12) for NO adsorption is liquid phase controlled and with an experimentally determined reaction rate constant being determined of $6.6 * 10^{-5}$.

Gas Phase Equilibrium

The gas phase portion of all three models utilizes a set of three equilibrium relations for NO, NO_2, N_2O_4, N_2O_3 and HNO_2 partial pressures. Expressions for their equilibrium constants follow standard format based upon their reaction mechanisms of;

$$2NO_2 \rightleftharpoons N_2O_4 \tag{13}$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \tag{14}$$

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \tag{15}$$

The equilibrium constants then are;

$$K_3 = \frac{P_3}{P_2^2} = 5.708 \tag{16}$$

$$K_4 = \frac{P_4}{P_1 * P_2} = 0.472 \tag{17}$$

$$K_5 = \frac{P_5^2}{P_1 * P_2 * P_{12}} = 1.284 \tag{18}$$

The values listed are those complied by Carta (1984). This group of equilibrium components are related to the NOx partial pressures by first defining chemical NO (NO^*) and chemical NO_2 (NO_2^*) (Sherwood et al., 1974);

$$NO^{*} = NO + N_2O_3 + 1/2HNO_2 \tag{19}$$

$$NO_2{}^{*} = NO_2 + 2N_2O_4 + N_2O_3 + 1/2\ HNO_2 \tag{20}$$

with NOx then defined by;

$$NOx = NO^{*} + NO_2{}^{*} \tag{21}$$

III. THEORETICAL

General

For this study the absorber models utilized consisted of packed towers filled with random dumped rings; these towers being described in Section III, Implementation. The absorption of NOx in the simulated towers utilized several common assumptions:

1. the NOx-Air mixture follows Ideal Gas behavior at the concentrations under consideration (see Appendix B);
2. the gas flow rate was considered to be constant for the low NOx concentrations involved in this study;
3. the absorption process for NOx is isothermal due to the low concentrations involved and the relatively large heat capacity of the water present (see Appendix D);
4. the partial pressure of water in the gas phase was assumed to be at 100% saturation for the prevailing temperature;
5. the absorption process in the tower can be represented by a series of difference calculations beginning at the bottom of the tower.

In considering the absorption of NOx the specific oxide form involved is critical. Considering NOx sources such as discussed in Section I the absorption process involves gaseous NO and NO_2 and other equilibrium related species. The equilibrium species that were considered in this study were N_2O_3, N_2O_4 and HNO_2. Other equilibrium relations such as with HNO_3 also exist but at levels that were considered insignificant for inclusion in this model. The species that were considered can be related to NOx by the definitions of chemical NO (NO^*) and chemical NO_2 (NO_2^*) as given in equations (19) and (20);

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

$$NO_2^* = NO_2 + 2N_2O_4 + N_2O_3 + 1/2HNO_2$$

With these relations for NO^* and NO_2^* being used to define NOx as in equation (21);

$$NOx = NO^* + NO_2^*$$

These representations of NO^*, NO_2^* and NOx were used as the absorbing species in the three models studied.

Water Absorption Model

Model A which describes the absorption of NOx into water is of major significance as it is the foundation for both the Sodium hydroxide and Hydrogen peroxide solution towers (Models B and C) as well as the basis of comparison for the study. This model is simular to that used by Counce (1980) to describe NOx absorption into packed towers; a schematic of this model is given in Figure (1).

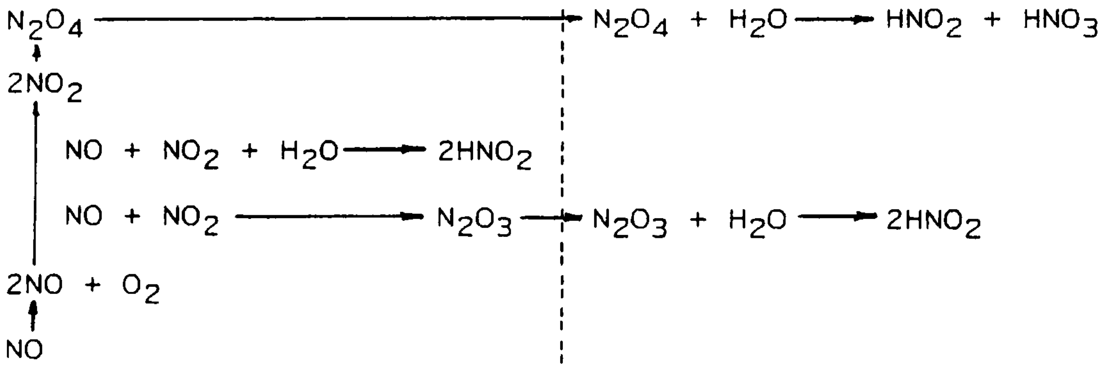

Figure 1. NOx absorption in water model.

In this model NOx absorption was considered in terms of NO^* and NO_2^*, the absorption flux terms for these species being definable as;

$$P_{10,o} = P_{10,i} - R_4 * \frac{a * \Delta V * R * T}{G} - P_1 * X_1 \qquad (22)$$

$$P_{11,o} = P_{11,i} - (2 * R_3 + R_4) * \frac{a * \Delta V * R * T}{G} + P_1 * X_1 \qquad (23)$$

Both equations (22) and (23) are in the form of the general material balance for a gas stream flowing through an incremental absorber section;

OUT = IN - ABSORPTION +(-) REACTION

The absorption flux terms for N_2O_4 and N_2O_3 the flux terms were given in equations (3) and (4) as;

$$R_3 = (H \sqrt{D * k})_3 * P_3$$

$$R_4 = (H \sqrt{D * k})_4 * P_4$$

Equations (3) and (4) are based upon experience that the absorption of N_2O_4 and N_2O_3 is usually liquid phase dependent in packed towers with the gas phase contribution being negligible. Where the absorption for the above species is normally liquid phase controlled HNO_2 absorption is generally gas phase transfer limited as result of its high solubility in water. In this model though its absorption is negligible due to the presence of the stronger acid HNO_3 which impedes its disassociation (Carta, 1984) and thus its absorption into water. The last species to be considered is NO which is of negligible importance to adsorption in this model. Though it is theoretically a factor for desorption from the absorber liquid its importance is again negligible in this model.

In equations (22) and (23) for NO^* and NO_2^* there is a reaction term included to account for the oxidation of NO to NO_2 via reaction (5);

$$2NO + O_2 \longrightarrow NO_2$$

with;

$$-r_1 = k * P_1^2 * P_9 \qquad (24)$$

Solution for the conversion of NO is then accomplished using techniques for evaluating a plug flow reactor such as given by Levenspiel (1972) which permits expressing the reaction rate in terms of conversion;

$$-r_1 = k * (P_1 * (1 - X_1))^2 * (P_9 * (1 - \frac{P_1}{P_9} * X_1)) \qquad (25)$$

Defining the material balance for an incremental segment for NO to be;

NO out = NO in - Disappearance by reaction

which assumes that no absorption of NO is occurring in the increment. This equation is then expressable in derivative form as;

$$\frac{G * P_{1,i}}{R * T} = \frac{G * P_{1,o}}{R * T} + \frac{-r_1}{R * T} dV \qquad (26)$$

Then upon integration and rearrangement of equation (26) as detailed by Counce (1980) a polynomial in X_{NO} is obtained;

$$X_1 = \frac{k * P_1 * P_9 * V}{G} - \frac{1}{1 + M} * \left(\frac{1}{1 - X_1} + \frac{M}{1 + M} * \ln \frac{1 + M * X_1}{1 - X_1} \right) \qquad (27)$$

where;

$$M = - \frac{P_1}{2 * P_9}$$

The gas-liquid interfacial area is important to the determination of NOx absorption. For this study it was assumed that the surface area of the packing was fully available for contacting so that the published values could be utilized in the model.

Sodium Hydroxide Absorption Model

Development of Model B for the absorption of NOx into an aqueous solution of Sodium hydroxide parallels that in Model A. This model is shown in Figure (2) in which the gas phase portion is identical to that of Model A with all liquid phase changes being related to the acid-base reactions;

$$HNO_2 + NaOH \longrightarrow NaNO_2 + H_2O \qquad (28)$$

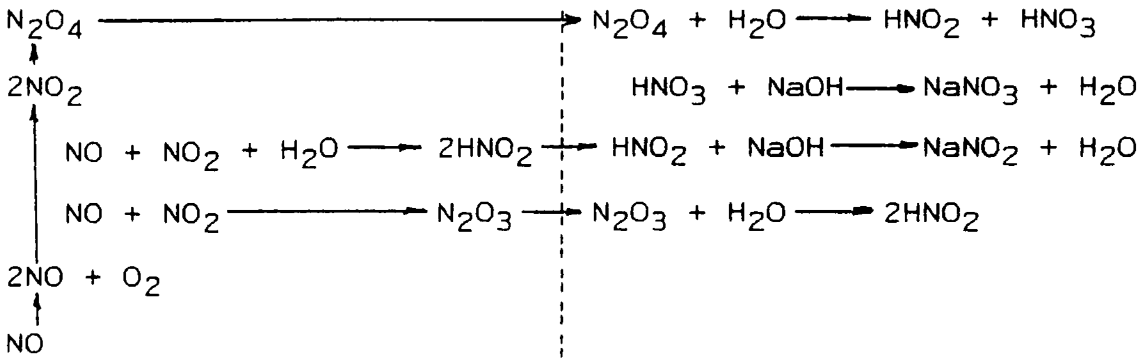

Figure 2. Model for NOx absorption in Sodium hydroxide solutions.

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O \qquad (29)$$

The first of two significant results of these reactions is that HNO_2 is removed from the absorber solution thus preventing the decomposition reaction;

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO \qquad (30)$$

The second result of these reactions is that as the stronger acid, HNO_3, is neutralized the major resistance to the absorption of the weaker acid HNO_2. This results in a significant flux for HNO_2 especially at low NOx partial pressures where N_2O_3 and N_2O_4 contributions tend to decrease (Carta, 1984). In a study by Carta (1984) a flux equation was proposed for HNO_2 based on the assumptions that an instantaneous irreversible reaction occurs at the interface and that the hydroxyl ion concentration at the interface is much larger than that of HNO_2. The resulting flux equation is then equation (7);

$$R_5 = k_{g5} * P_5 + \frac{D_5 * K}{2 * R * T * k_{g5}} * P_1 * P_2 * P_{12}$$

Besides the two flux changes mentioned Model B is simular to Model A in all other aspects. This includes an assumption that flux terms for N_2O_4 and N_2O_3 are not affected by the concentration of nitrates and nitrites in the dilute absorbing solution. Based on the assumption that the equations developed for Model A apply with only the addition of a flux term for HNO_2 give absorption equations for NO^* and NO_2^* of;

$$P_{10,o} = P_{10,i} - (R_4 + {}^1/_2 * R_5) * \frac{a * \Delta V * R * T}{G} - P_1 * X_1 \qquad (31)$$

$$P_{11,o} = P_{11,i} - (2 * R_3 + R_4 + {}^1/_2 * R_5) * \frac{a * \Delta V * R * T}{G} + P_1 * X_1 \qquad (32)$$

Hydrogen Peroxide Absorption Model

Model C for the absorption of NOx into an aqueous Hydrogen peroxide solution again is a modification of the Model A with three changes in flux equations being required. A system outline is given in Figure (3) which shows these changes which can be compared to Model A.

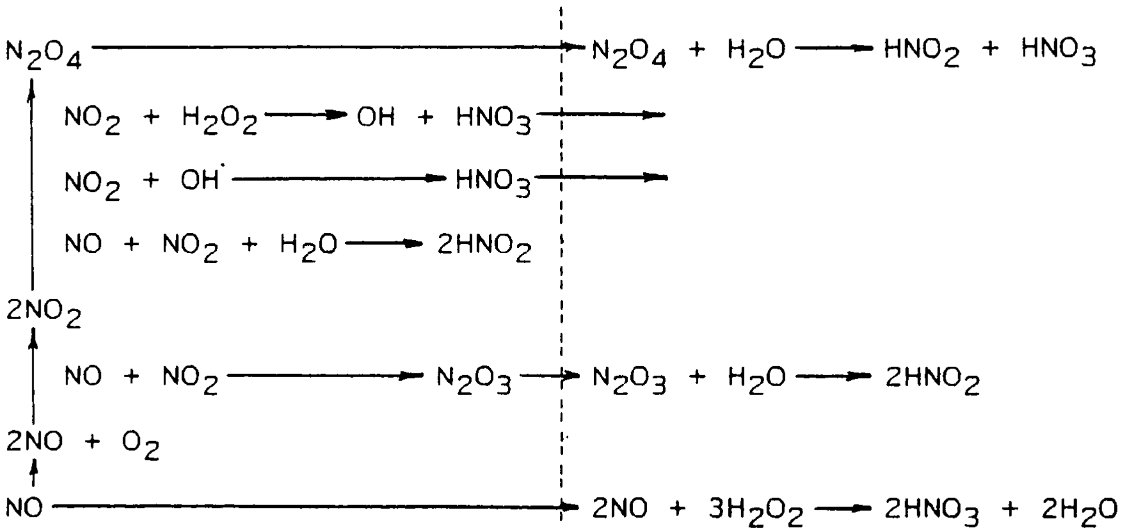

Figure 3. Model for NOx absorption in Hydrogen peroxide solutions.

In this model a reaction between Hydrogen peroxide and NO_2 in the gas phase of the absorber is added. In a study of the gas phase reactions between NO_2 and H_2O_2 Gray et al. (1972) determined that this reaction is significant at H_2O_2 partial pressures above 0.2 ppm. This study further presented the reaction as actually involving reactions (10) and (11) with reaction (10) being the rate controlling step.

$$NO_2 + H_2O_2 \longrightarrow HNO_3 + OH^-$$

$$NO_2 + OH^- \longrightarrow HNO_3$$

As these reactions occur in the gas phase a similar technique as shown by Counce (1980) for the oxidation of

NO to NO_2 was utilized to calculate a NO_2 conversion. The conversion calculated as shown in Appendix C is then added to the NO_2^* absorption equation as is the NO oxidation to NO_2 term. In this case the adjustment is negative resulting in a modification to equation (23) for NO_2^* of;

$$P_{11,o} = P_{11,i} - (2 * R_3 + R_4) * \frac{a * \Delta V * R * T}{G} + P_1 * X_1 - P_2 * X_2 \qquad (33)$$

It is also assumed in this model that that the NO_2-H_2O_2 reaction is irreversible and all HNO_3 present is absorbed as it is produced.

Both gas phase and liquid phase reactions exist for NO with H_2O_2. The rate constant for the gas phase was determined by Gray (1972) and was considered to be negligible for purposes of this study while a liquid phase reaction of NO with H_2O_2 via;

$$2NO + 3H_2O_2 \longrightarrow 2HNO_3 + 2H_2O \qquad (34)$$

does provide a contribution to NOx absorption. This mechanism was proposed by Baveja (1979) as an empirically based expression with the absorption flux for NO into Hydrogen peroxide solutions of stated in equation (12) as;

$$R_1 = S_1 * \sqrt{D_1 * k} * \sqrt{C_g}$$

This is then used in the NO* absorption equation of;

$$P_{10,o} = P_{10,i} - (R_1 + R_4) * \frac{a * \Delta V * R * T}{G} - P_1 * X_1 \qquad (35)$$

Gas Phase Equilibrium

The models must also account for the series of equilibrium relationships that exist between the gas phase components of NOx. Included in these relationships are the NO and NO_2 oxidation reactions discussed previously which were assumed to be irreversible for this development.

The group of equilibrium reactions important to NOx absorption are reactions (13) through (15);

$$2NO_2 \longleftrightarrow N_2O_4$$

$$NO + NO_2 \longleftrightarrow N_2O_3$$

$$NO + NO_2 + H_2O \longleftrightarrow 2HNO_2$$

with the equilibrium relationships as defined in equations (16) through (18);

$$K_3 = \frac{P_3}{P_2^2}$$

$$K_4 = \frac{P_4}{P_1 * P_2}$$

$$K_5 = \frac{P_5^2}{P_1 * P_2 * P_{12}}$$

As these relationships are more useful when solved for the products of reactions (13), (14) and (15) they may be rearranged to give;

$$P_3 = K_5 * P_2^2 \tag{36}$$

$$P_4 = K_4 * P_1 * P_2 \tag{37}$$

$$P_5 = \sqrt{K_5 * P_1 * P_2 * P_{12}} \tag{38}$$

These equations then may be substituted into equations (19) and (20) for the calculation of NO^* and NO_2^* as functions of the partial pressures of NO and NO_2;

$$P_{10} = P_1 + K_4 * P_1 * P_2 + {}^1/_2 * \sqrt{K_5 * P_1 * P_2 * P_{12}} \tag{39}$$

$$P_{11} = P_2 + 2 * K_3 * P_{22} + K_4 * P_1 * P_2 + {}^1/_2 * \sqrt{K_5 * P_1 * P_2 * P_{12}} \tag{40}$$

If reaction (21) for NOx is then restated in terms of partial pressures a set of three equations in two unknowns is obtained;

$$P_{13} = P_{10} + P_{11} \tag{41}$$

Using these last three equations was shown by Counce (1980) to provide the basis for calculating the equilibrium partial pressures for NO and NO_2 at given NOx (P_{13}), NO^* (P_{10}) and NO_2^* (P_{11}) levels. Upon solution of these three equations for the two unknowns equations (36) through (38) may be used to obtain new equilibrium partial pressures for the N_2O_3, N_2O_4 and HNO_2. For these equations constant water and oxygen partial pressures were assumed.

IV. IMPLEMENTATION

To accomplish the objective of this study absorption evaluations for all three models had to be performed at several points. For these evaluations a standard absorption tower was defined using the parameters of Table (1) with a series of inlet NOx concentrations and NO/NO_2 ratios. These parameters were the inputs to a BASIC program utilizing the three models developed to determine the exit NOx, NO^* and $NO_2{}^*$ concentrations.

The program (reference Appendix E) approach is outlined in the flow sheet in Figure (4). In this program once the inlet equilibrium conditions were established the simulations for Models B, C then A were performed. In these simulations the NOx absorption was determined by using the material balance equations developed for the individual models. As these equations are dependent upon the NOx component (NO, NO_2, N_2O_4 etc.) concentrations after each absorption calculation the equilibrium state must be determined. To accomplish this equations (39) through (41) were simultaneously solved for NO and NO_2 using the Complex Method of Box with penalty functions. This technique results in the new values for NO and NO_2 being at the same NOx, NO^* and $NO_2{}^*$ levels as at the end of the last absorption calculation. These new NO and NO_2 values were then used in equations (36) through (38) to

Table 1. Fixed column conditions

Parameter	Value
Gas flow	$3.3 * 10^4$ cm^3/s
Liquid flow	$1.3 * 10^2$ cm^3/s
Tower diameter	16.2 cm
Tower area	204.8 cm^2
Packing size	1.59 cm (0.63 in)
Packing type	Dumped Glitsch Ballast Rings
System temperature	300 K
System pressure	0.97 atm (740 mmHg)
Sodium hydroxide concentration	3% by weight
Hydrogen peroxide concentration	3% by weight

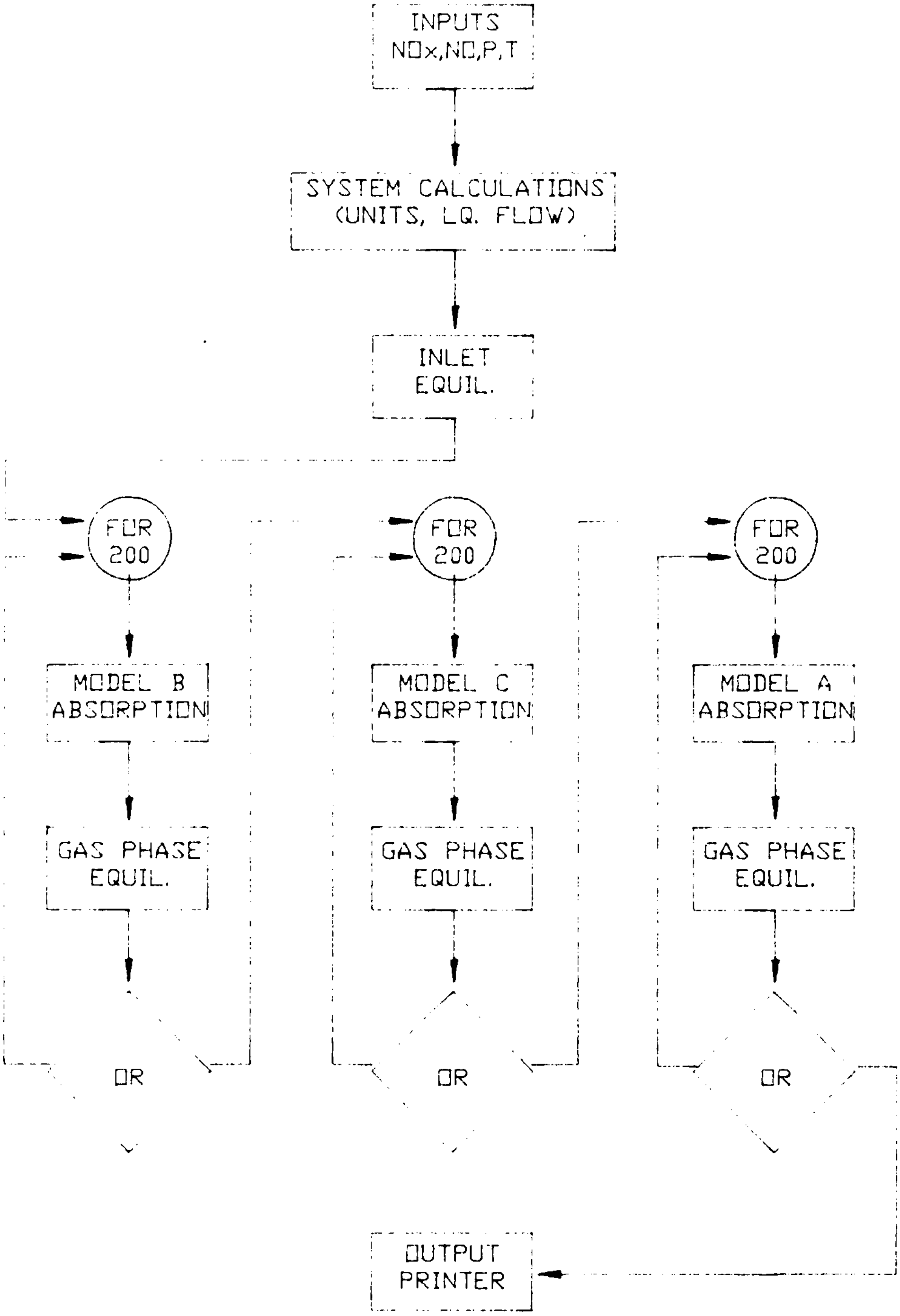

Figure 4. Computer program flow sheet.

determine the new N_2O_3, N_2O_4 and HNO_2 concentrations. This procedure was followed for all three models over the assumed 200 cm packing height in 1 cm increments.

All program development and execution was accomplished using HP BASIC on a Hewlett-Packard model 86A personal computer.

V. RESULTS

In the current study the computer program in Appendix D was run a total of nine times with results being obtained for each of the three absorber models in each run. For each of these program runs the absorber conditions listed in Table (1) were utilized at a range of inlet NOx concentrations and NO to NO_2 ratios. The program then calculated exit NOx, NO^*, NO_2^* and reagent usage (Sodium hydroxide or Hydrogen peroxide). This data and the NOx conversion percentages calculated from it are presented in Table (2).

Review of the results obtained lead to several observations of importance:

1. NOx conversion was concentration dependent as indicated in the literature for the water system but also for the Sodium hydroxide and Hydrogen peroxide solution systems;

2. the NOx conversion dependency on the NO to NO_2 ratio was also observed for all solutions;

3. the addition of either Sodium hydroxide or Hydrogen peroxide is effective in improving the NOx conversion;

4. a reduction in the absorption levels was noted as the percent NO was increased indicating that NOx absorption is primarily as NO_2^*.

Table 2. Tower exhaust summary

INLET	NOx (atm * E04)	2.921	4.868	4.868	4.868	9.737	9.737	9.737	97.37	97.37	194.7	194.7	292.1	292.1
CONDITIONS	NO (%)	25	25	50	75	25	50	75	25	50	25	50	25	50
WATER	NOx (atm * E04)	2.896	4.799	4.734	4.857	9.466	9.602	9.691	78.17	86.41	135.6	157.1	182.7	215.9
ABSORBER	NO* (atm * E04)	0.729	1.214	2.427	3.641	2.420	4.840	7.259	23.07	45.27	43.80	81.86	62.27	109.1
RESULTS	NO$_2^*$ (atm * E04)	2.167	3.585	2.407	1.216	7.046	4.762	2.432	55.10	41.41	91.80	75.21	120.4	106.8
(MODEL A)	NOx Conversion (%)	0.8	1.4	0.7	0.2	2.8	1.4	0.5	19.7	11.3	30.4	19.3	37.5	26.1
SODIUM	NOx (atm * E04)	2.873	4.737	4.808	4.851	8.604	9.493	9.667	67.41	80.49	110.5	141.0	144.4	188.7
HYDROXIDE	NO* (atm * E04)	0.729	1.213	2.427	3.641	2.420	4.840	7.258	23.06	45.22	43.87	81.75	62.47	108.9
ABSORBER	NO$_2^*$ (atm * E04)	2.144	3.524	2.381	1.210	6.184	4.653	2.409	44.35	35.27	66.62	59.30	81.92	79.75
RESULTS	NOx Conversion (%)	1.6	2.7	1.2	0.3	11.6	2.5	0.7	30.8	17.3	43.2	27.6	50.6	35.4
(MODEL B)														
HYDROGEN	NOx (atm * E04)	2.868	4.729	4.803	4.849	9.220	9.501	9.664	67.49	81.66	110.9	141.7	145.2	190.1
PEROXIDE	NO* (atm * E04)	0.729	1.213	2.427	3.641	2.420	4.839	7.259	23.15	46.35	44.17	82.18	63.06	109.7
ABSORBER	NO$_2^*$ (atm * E04)	2.139	3.516	2.376	1.208	6.799	4.662	2.405	44.34	33.31	66.70	59.57	82.15	80.39
RESULTS	NOx Conversion (%)	1.8	2.9	1.3	0.4	5.3	2.4	0.8	30.7	16.1	43.0	27.2	50.3	34.9
(MODEL C)														

Additional program runs were performed as well to verify the base water absorber model (model A) against a known results. For this comparison experimental points reported by Counce (1980) were selected. The point used from that study were numbers 10-27, 10-29 and 10-31. The results from this comparison are given in Table (3) which demonstrate a good match between calculated and experimental values.

Table 3. Comparison of Model A to experimental data

	10-27 EXPERIMENTAL DATA	MODEL RESULTS	10-29 EXPERIMENTAL DATA	MODEL RESULTS	10-31 EXPERIMENTAL DATA	MODEL RESULTS
INLET NOx (atm)	0.0464	0.0464	0.0506	0.0506	0.0528	0.0528
EXIT NOx (atm)	0.0076	0.0077	0.0165	0.0155	0.0121	0.0112
NOx CONVERSION (%)	83.7	83.4	67.4	69.4	77.1	78.8

VI. CONCLUSIONS

As shown in Section V the results obtained from the models indicate a significant improvement in the absorption of NOx into Models B and C as compared to that for Model A. While the improvement was noted a strong dependency of Models B and C on Model A is obvious as the three curves in Figure (5) are similar in appearance.

These observations are the result of the dependency of all three models on the absorption of N_2O_4 and N_2O_3 into water. It is important to note that the absorption of both components are independent of reactions with Sodium hydroxide or Hydrogen peroxide and represent the only mechanisms for absorption used in Model A. For Model B the increased absorption is due to the absorption of HNO_2 (equation 7) while for Model C the enhancement is the result of the absorption/reaction of NO (reaction 34) and the reaction of NO_2 with Hydrogen peroxide (reactions 10 and 11) with the subsequent absorption of HNO_3. It can be further concluded that the increase in NOx absorption in Model C was primarily due to the NO_2-H_2O_2 reaction based on the absorption response to higher NO levels in the input.

As predicted in the literature regarding absorption in Sodium hydroxide solutions (Carta, 1984) the relating importance of HNO_2 absorption increases at lower

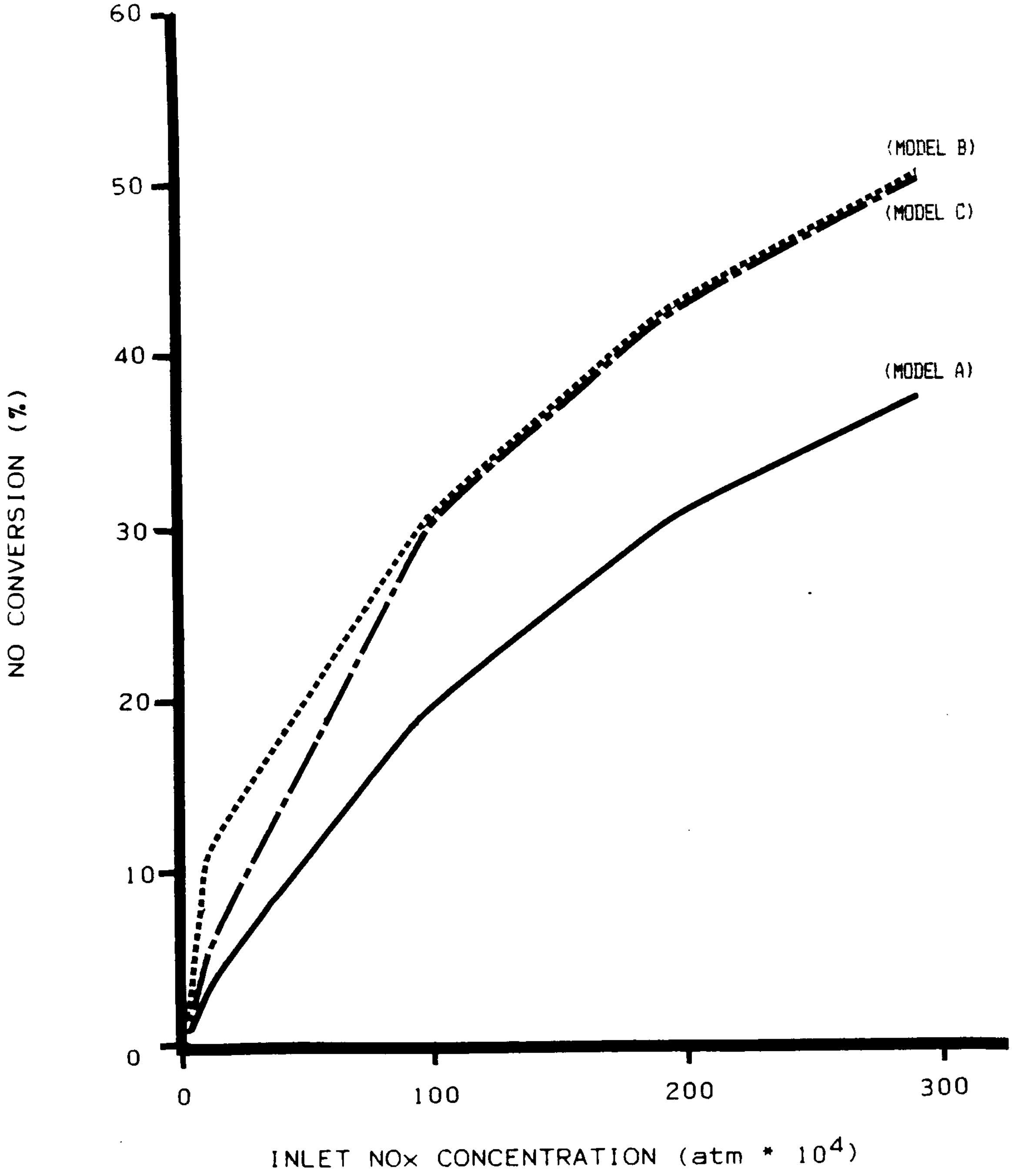

Figure 5. NOx reduction summary for 25% NO in inlet evaluations.

concentrations. This is evidenced by the ratio of the conversion of NOx in Model B to that in Model A which at 292 * 10^{-4} atm inlet NOx is 1.35 while at an inlet NOx of 4.9 * 10^{-4} atm this ratio is increased to 1.93. The improvement parameters are also of increased importance in Model C at lower NOx concentrations as evidenced by the NOx conversion ratio of Model C to Model A. In this case the ratio at a NOx inlet of 292 * 10^{-4} atm is found to be 1.34 whereas at 4.9 * 10^{-4} atm the ratio is 2.07.

Important to these conclusions are the observations pertaining to the accuracy of the models. As Model A is the base model for B and C its validity is of key importance. This validity was substantiated by the comparison to the experimental points reported by Counce (1980) in which the calculated NOx conversions were less than 3% above the experimental values. From this result the validity of Models B and C may be inferred as they are built upon Model A. Further support to Model A was also given by the observed importance the inlet NOx and NO levels in the system as observed by Counce (1980). Additional verification for Model B was accomplished by noting the increased importance of the absorption of HNO_2 at lower NOx concentrations as reported by Carta (1984).

LIST OF REFERENCES

Barish, N.N., S. Kaplan, "Economic Analysis for Engineering and Managerial Decision Making,"2 Ed., McGraw-Hill Book Co. (1978)

Baveja, K.K., D. Subba Rao and M.K. Sarkar, "Kinetics of Absorption of Nitric Oxide in Hydrogen Peroxide Solutions," Journal of Chemical Engineering of Japan, 12(4), p.322 (1979)

Bennett, C.O., J.E. Myers, "Momentum, Heat and Mass Transfer," 2 Ed., McGraw-Hill Book Co. (1974)

Carta, G., "Role of HNO_2 in the Absorption of Nitrogen Oxides in Alkline Solutions," Ind. Eng. Chem. Fundam., 23(2), p.260 (1984)

Castellan, G.W., "Physical Chemistry," 2 Ed., Addison-Wesley Publishing Co. (1971)

Chen, G.K., "Packed Column Internals," Chemical Engineering, March 5,1984, p.40

Counce, R.M., "Nitrogen Oxide Absorption into Water and Dilute Nitric Acid in an Engineering-Scale Sieve-Plate Column - Description of a Mathematical Model and Compairson with Experimental Data," Oak Ridge National Laboratory (1978)

Counce, R.M., "The Scrubbing of Gaseous Nitrogen Oxides in Packed Towers," Oak Ridge National Laboratory (1980)

Counce, R.M., J.J. Perona, "A Mathematical Model for Nitrogen Oxide Absorption in a Sieve-Plate Column," I&EC Process Design & Development, 19(3), p.426 (1980)

Counce, R.M., J.J. Perona, "Scrubbing of Gaseous Nitrogen Oxides in Packed Towers," AIChE Journal, 29(1), p.26 (1983)

Esso Research and Engineering Co., "Development of the Aqueous Processes for Removing NO_2 from Flue Gases," NTIS (1972)

Glitsch, Inc., "Tower Packings and Internals," Bulletin Number 217, 3 Ed. (1983)

Gray, D., E. Lissi, J. Heicklen, "The Reaction of Hydrogen Peroxide with Nitrogen Dioxide and Nitric Oxide," The Journal of Physical Chemistry, 76(14), p.1919 (1972)

Harrington, C.D., A.E. Ruehle Editors, "Uranium Production Technology," D. Van Nostrand Co. (1959)

Henley, E.J., J.D. Seader, "Equilibrium-Stage Separation Operations in Chemical Engineering," John Wiley & Sons (1981)

Himmelblau, D.M., "Basic Principles and Calculations in Chemical Engineering," 3 Ed., Prentice-Hall Inc. (1974)

Hirsch, P.M., "Selected Conversion of NOx by Catalytic Reduction with Ammonia," Environmental Progress, 1(1), p.24, (1982)

Hoftyzer, P.J., J.G. Kwanten, "Processes for Air Polution Control," 2 Ed., Chemical Rubber Company (1972)

Howard, C.J., "Kinetic Study of the Equilbrium $HO_2+NO=OH+NO_2$ and the Thermochemistry of HO_2," J. Am. Chem. Soc., 102(23), p.6937 (1980)

Interel Corp., "Control of Nitrogen Oxide Emissions from Reactions of Metals with Nitric Acid, A Multi-Client Study" (1982)

Karlsson, H.T. et. al., "Control of NOx in Steel Pickling," Enviromental Progress, 3(1), p.40 (1984)

Krishnamurthy, R., R. Taylor, "Simulation of Packed Distillation and Absorption Columns," Industrial & Engineering Chemistry Process Design and Development, 24(3), p.513 (1985)

Levenspiel, O., "Chemical Reaction Engineering," 2 Ed., John Wiley & Sons Inc. (1972)

McCabe, W.L., J.C. Smith, "Unit Operations of Chemical Engineering," 3 Ed., McGraw-Hill Book Co. (1976)

Nagel, O., B. Hegner, H. Kurten, "Criteria for the Selection and Design of Gas/Liquid Reactors," International Chemical Engineering, 21(2), p.161 (1981)

Onda, K., E. Sada, H. Takeuchi, "Gas Absorption with Chemical Reaction in Packed Columns," Journal of Chemical Engineering of Japan, 1(1), p.62 (1968)

Onda, K., H. Takeuchi, Y. Okumoto, "Mass Transfer Coefficents Between Gas and Liquid Phases in Packed Columns," Journal of Chemical Engineering of Japan, 1(1), p.56 (1968)

Perry, R.H., D.W. Green, J.O. Maloney Editors, "Perry's Chemical Engineers' Handbook," 6 Ed., McGraw-Hill Book Co. (1984)

Peters, M.S., K.D. Timmerhaus, "Plant Design and Economics for Chemical Engineers," 3 Ed., McGraw-Hill Book Co. (1980)

Prausnitz, J.M., "Molecular Thermodynamics of Fluid-Phase Equilibrium," Prentice-Hall Inc. (1969)

Reed, R.C., J.M. Prausnitz, T.K. Sherwood, "The Properties of Gases and Liquids," 3 Ed., McGraw-Hill Book Co. (1977)

Reed, R.D., "Nitrogen Oxides Problems in Industry," Chemical Engineering, 84(22), p.153, (1977)

Schweitzer, P.A. Editor, "Handbook of Separation Techniques for Chemical Engineers," McGraw-Hill Book Co. (1979)

Sherwood, T.K., R.L. Pigford, D.R. Wilke, "Mass Transfer," McGraw-Hill Book Co. (1975)

Smith, J.M., H.C. VanNess, "Introduction to Chemical Engineering Thermodynamics," McGraw-Hill Book Co. (1975)

Treybal, R.E., "Mass Transfer Operations," 3 Ed., McGraw-Hill Book Co. (1980)

Wark, K., C.F. Warner, "Air Pollution Its Origin and Control," Thomas Y. Crowell Co. (1976)

APPENDIXES

APPENDIX A

LIST OF SYMBOLS

a	Liquid-gas interfacial area, (cm^2/cm^3)
A	Cross sectional area of tower, (cm^2)
C_j	Concentration of component j, ($gmol/cm^3$)
D_p	Nominal packing size, (cm)
D_j	Diffusivity of component j, (cm/s)
f_i	Fugacity of component i, (atm)
F	Molar flow, (gmol/s)
G	Volumetric gas flow rate, (cm^3/s)
h	Height of an increment, (cm)
H_j	Henry's Law coefficient for component j, ($gmol/cm^3$-atm)
$k_{G,j}$	Gas phase mass transfer coefficient for component j,(gmol/cm-atm-s)
k	Reaction rate coefficient, (1/s)
K_j	Equilibrium constant for reaction j, (1/atm)
L	Volumetric liquid flow rate, (cm^3/s)
M_j	Molecular weight of component j, (g/gmol)
n_j	Moles of component j, (gmol)
NOx	Nitrogen oxides
NO^*	Chemical NO
$NO_2{}^*$	Chemical NO_2
p	System pressure, (atm)
p_j	Partial pressure of component j, (atm)
r_j	Reaction rate for component j, ($gmol/cm^3$-s)
R	Gas constant, 82.1 (atm-cm^3/gmol-K)
R_j	Absorptive flux for component j, ($gmol/cm^2$-s)
S_j	Solubility of component j, ($gmol/cm^3$)

T	Temperature, (K)
v	Volumetric flow, (cm^3/s)
v_i	Partial molar volume of component i, (cm^3)
V	Volume, (cm^3)
x_j	Mole fraction of component j in liquid
X_j	Conversion of component j
y_j	Mole fraction of component j in gas
Z	Compressibility of gas phase

Subscripts

1	NO
2	NO_2
3	N_2O_4
4	N_2O_3
5	HNO_2
6	HNO_3
7	NaOH
8	H_2O_2
9	O_2
10	NO^*
11	NO_2^*
12	H_2O
13	NOx
c	Critical property
i	Component or input
j	component or reaction

o	output
T	Total

Greek Symbols

Δ	Difference between two values, typically initial and final
ε	Fractional volume change
Ω	Constant
φ	Fugacity Coefficient
τ	Space-time, (s)

APPENDIX B

JUSTIFICATION OF IDEAL GAS BEHAVIOR ASSUMPTIONS

In the model presented it has been assumed that the gases follow Ideal Gas behavior rules in all regions of the absorbers. This fundamental assumption was used to simplify the model by permitting usage of these gas mixture relationships:

1. Dalton's Law of partial pressures: The total system pressure is the sum of all component partial pressures in the system. In addition the ratio of a specific partial pressure to the total pressure is equal to the mole fraction of the component, or;

$$p_T = \sum p_i \tag{B.1}$$

$$\frac{p_i}{p_T} = \frac{n_i}{p_T} = y_i \tag{B.2}$$

2. Amagat's law of partial volumes: In this parallel relationship the sum of component volumes is equal to the volume of the mixture, or;

$$V_T = \sum V_i \tag{B.3}$$

$$\frac{V_i}{V_T} = \frac{n_i}{n_T} = y_i \tag{B.4}$$

Usage of these relationships was the basis of equating the parts per million (ppm) component concentration to the component mole fraction. This equality greatly simplifies the model as inlet concentrations are always given in ppm while the absorption calculations require partial pressure values which then need to be converted to ppm values for reporting of exhaust concentrations.

Verification of this assumption begins with the ideal gas equation of state with compressibility factor which is accepted as;

$$p * V = Z * n * R * T \tag{B.5}$$

For this equation to describe a truly ideal gas the compressibility factor (Z) and the fugacity coefficient (φ) must equal one. The fugacity coefficient being defined as;

$$\varphi_i = \frac{f_i}{y_i * p_T} \tag{B.6}$$

with Dalton's law of

$$y_i * p_T = p_i \tag{B.7}$$

then

$$f_i = p_i \qquad \text{for} \qquad \varphi = 1$$

To verify the assumption of the fugacity coefficient and compressibility factor equaling one the Redlich-Kwong equation of state was used to calculate these terms for the mixture components. This equation of state has the form of;

$$Z = \frac{v}{v - b} - \frac{a}{R * T^{1.5} * (v + b)} = \frac{p * V}{n * R * T} \qquad (B.8)$$

where 'a' and 'b' are found using Redlich's proposed composition dependencies;

$$a = \sum_{i} \sum_{j} y_1 * y_j * a_{ij} \qquad (B.9)$$

$$a_{ij} = \sqrt{a_i * a_j} \qquad (B.10)$$

$$b = \sum y_1 * b_i \qquad (B.11)$$

with component values defined as;

$$a_i = \Omega_a * R^2 * T_c^{2.5} * p_c^{-1} \qquad (B.12)$$

$$b_i = \Omega_b * R * T_c * p_c^{-1} \qquad (B.13)$$

This solution is a simplified form of a more complex equations that have been modified by accepting the critical temperature (T_C), critical pressure (P_C) and acentric factor to be independent of concentration in the regime under consideration.

Once the compressibility factor (Z) is calculated using Redlich-Kwong a proposed modification by Chueh may be utilized to obtain the fugacity coefficient, this equation is given as;

$$\ln \varphi_k = \ln \frac{v}{v - b} + \frac{b_k}{v - b} - \frac{2 * \Sigma y_i * a_i}{R * T^{1.5} * b} * \ln \frac{v - b}{v} + \frac{a * b_k}{R * T^{1.5} * b^2} * \left(\ln \frac{v - b}{v} - \frac{v}{v + b} \right) - \ln \frac{p * v}{R * T} \qquad (B.14)$$

Solution of these equations was then performed as to evaluate the ideality of a NOx and air system at ambient conditions assuming the NOx mixture considered to be a combination of the major components of NOx; NO, NO_2 and N_2O_4. Five evaluations on this system were performed producing results (reference Table 4) which demonstrate that the compressibility factor and component fugacity coefficients satisfy the requirements for using the ideal gas law for the dilute NOx in air system.

Table 4. Fugacity coefficients and compressability factors for NOx in air mixtures

	y	φ	y	φ	y	φ	y	φ	y	φ
NITROGEN	0.785	0.99904	0.785	0.9903	0.785	0.99901	0.785	0.9995	0.785	0.99933
OXYGEN	0.21	0.99866	0.21	0.99866	0.21	0.99863	0.21	0.99924	0.21	0.9990
NITROGEN OXIDE	0.0025	0.99838	0.005	0.99837	0	-	0.0025	0.99905	0.0025	0.99784
NITROGEN DIOXIDE	0.001	0.99574	0.004	0.99573	0.005	0.99568	0.001	0.99736	0.001	0.99648
NITROGEN TETROXIDE	0.0015	0.99389	0.001	0.99387	0.005	0.99381	0.0015	0.99615	0.0015	0.99487
TEMPERATURE [K]	293		293		293		310		310	
PRESSURE [atm]	1		1		1		0.75		1	
Z		1		1		1		1		1

APPENDIX C

REACTION OF NO_2 WITH H_2O_2

For the reactions given in equations (10) and (11);

$$NO_2 + H_2O_2 \longrightarrow HNO_3 + OH^-$$

$$NO_2 + OH^- \longrightarrow HNO_3$$

an incremental conversion (X_2) may be calculated in a method similar to that used for the oxidation of NO to NO_2.

Considering the absorber as a ideal plug flow reactor the standard model is;

$$\frac{V}{F_{Ao}} = \int \frac{dX_A}{-r_A} \qquad (C.1)$$

for which in a series of small reactors;

$$X_{A,1} = 0$$

and

$$X_{A,2} = X_A < 0.0001$$

The assumption of $X_A < 0.0001$ permits treatment as a constant volume system with;

$$\varepsilon_A \approx 0$$

Working with the reaction (10) only at this point the reaction rate expression is;

$$-r_A = k * C_A * C_B \tag{C.2}$$

where the subscripts are defined as;

$A = NO_2$

$B = H_2O_2$

Defining;

$$C_A = C_{Ao} - C_{Ao} * X_A \tag{C.3}$$

$$C_B = C_{Bo} - C_{Bo} * X_B \tag{C.4}$$

with

$$C_{Ao} * X_A = C_{Bo} * X_B \tag{C.5}$$

upon substitution and rearrangement gives;

$$-r_A = k * C_{Ao}^2 * (1 - X_A) * (M - X_A) \tag{C.6}$$

where

$$M = \frac{C_{Bo}}{C_{Ao}} \qquad (C.7)$$

Substituting equation (C.6) into equation (C.1) gives;

$$\frac{V}{F_{Ao}} = \int \frac{dX_A}{k * C_{Ao}^2 * (1 - X_A) * (M - X_A)} \qquad (C.8)$$

which then simplifies to;

$$\frac{k * C_{Ao}^2 * V}{F_{Ao}} = \int \frac{dX_A}{(1 - X_A) * (M - X_A)} \qquad (C.9)$$

This may then be reduced further by using the basic relations of;

$$\frac{V}{F_{Ao}} = \frac{\tau}{C_{Ao}} \qquad (C.10)$$

and

$$\tau = \frac{V}{v_o} \qquad (C.11)$$

which when combined and simplified gives;

$$\frac{V}{F_{Ao}} = \frac{V}{v_o * C_{Ao}} \qquad (C.12)$$

$$F_{Ao} = v_o * C_{Ao} \qquad (C.13)$$

The substitution of this result back into equation (C.9) then gives;

$$\frac{k * C_{Ao} * V}{v_o} = \int \frac{dX_A}{(1 - X_A) * (M - X_A)} \qquad (C.14)$$

which is an integral in the general form of;

$$\int \frac{dx}{u * v} = \frac{1}{k} * \ln\left(\frac{u}{v}\right) \qquad (C.15)$$

where

$x = X_A$

$u = a + b * x = 1 - X_A$

$v = c + d * x = M - X_A$

$k = a * b - c * d = M - 1$

which upon integration is;

$$\frac{k * C_{Ao} * V}{v_o} = \frac{1}{M - 1} * \ln\left(\frac{M - X_A}{1 - X_A}\right) \qquad (C.16)$$

Rearrangement of equation (C.16) produces a function for X_A may be solved directly;

$$X_A = \frac{M * \left(\exp\left[\frac{k * C_{Ao} * (M - 1)}{v_o}\right] - 1\right)}{M * \left(\exp\left[\frac{k * C_{Ao} * (M - 1)}{v_o}\right]\right) - 1} \qquad (C.17)$$

The result from equation (C.17) is the conversion for reaction (10) only which is the rate determining step for the sequence (Gray, 1972). In determining the conversion for both steps it may be assumed that reaction (11) is instantaneous in comparison to reaction (10). This then permits setting the overall conversion to equal twice the conversion of reaction (10) as the additive effect of these reactions is the conversion of two moles of NO_2 per mole of H_2O_2.

APPENDIX D

VERIFICATION OF ISOTHERMAL CONDITIONS

In all absorption models used in this study isothermal conditions were assumed to exist. To verify this assumption the heats of formation for the involved compounds were used to determine heats of reaction for the primary reactions involved in Model B. Utilizing heat of formation data from Perry's 5th edition (1973) these heats of reaction were obtained in kcal/gmole;

N_2O_4-H_2O	-3.81	(D.1)
HNO_2-OH^-	-10.73	(D.2)
HNO_3-OH^-	-21.66	(D.3)
N_2O_3-H_2O	-8.68	(D.4)
NO_2 TO N_2O_4	-13.15	(D.5)
NO-NO_2	-9.29	(D.6)

Using the absorption models for N_2O_3 and N_2O_4 only for the absorption of NOx as a simplification to give an order of magnitude answer first gives total heats for each of;

$$N_2O_3 \text{ heat} = (D.6)+(D.4)+2*(D.2) = -39.43 \qquad (D.7)$$

$$N_2O_4 \text{ heat} = (D.5)+(D.1)+(D.2)+(D.3) = -49.35 \qquad (D.8)$$

Then assuming that half of the NOx absorption follows N_2O_3

with the rest as N_2O_4 gives a NOx heat of -44.39 kcal/gmole.

Selecting for a test point that run with the highest NOx absorption in which 147.7 atm was removed a maximum temperature rise can be estimated. Using the Ideal gas law and the empty tower volume of 40.95 l the NOx removal is converted to 0.0246 gmoles. Then by using a standard equation for temperature rise <u>vs</u>. heat input;

$$q = m * C_p * \Delta T \qquad (D.9)$$

Which for the case selected is;

$$(0.0246 \text{ gmole})(44.39 \text{ kcal/gmole}) = (11{,}135 \text{ g})(0.001 \text{ cal/g-deg})(\Delta T) \qquad (D.10)$$

The result of which is a temperature rise of 0.098 degrees which is insignificant in comparison to the 300 K operation point.

APPENDIX E

LISTING OF COMPUTER PROGRAM

```
1000 CLEAR
1010 DISP "NOx ABSORBER EFFECTIVENESS PROGRAM; CALCULATES OUTPUTS"
1020 DISP "    FROM WATER, SODIUM HYDROXIDE SOLUTION AND"
1030 DISP "    HYDROGEN PEROXIDE SOLUTION ABSORBERS."
1040 DISP
1050 REM THIS PROGRAM IS PART OF A THESIS PROJECT FOR THE MSChE DEGREE
1060 REM     FROM THE UNIVERSITY OF TENNESSEE, KNOXVILLE.
1070 REM      TRACY J. COATES, P.E.; DECEMBER 1986
1080 ! ////////////////////////////////////////////////////////////////////////
1090 RANDOMIZE
1100 WAIT 3000
1110 GOSUB DINPT  ! DIVERTS TO DATA INPUT SUBROUTINE+++++++++++++++++++++++++++
1120 GOSUB EMCONC  ! EMISSION STANDARD CALCULATION++++++++++++++++++++++++++++
1130 GOSUB UNITS  ! METRIC/ENGLISH UNIT CONVERSION ROUTINE++++++++++++++++++++
1140 dh=1 ! INCREMENTAL STEPSIZE THROUGH TOWERS; [cm]
1150 ! ////////////////////////////////////////////////////////////////////////
1160 REM DEFINE MATRICES FOR PROGRAM AND SUBROUTINES
1170 DIM P(6),CPNOX(2,5000) ! MAIN PROGRAM
1180 DIM AH2O2(5000),XFN(50),XNO(50) ! TOWER CALCULATIONS
1190 DIM DX(2),OB(5),RKK(5,2),RKL(2),RC(2),RT(2),RV(2) ! EQUIL SUBROUTINE
1200 ! ////////////////////////////////////////////////////////////////////////
1210 REM EQUILBRIUM CONSTANTS, GAS PHASE
1220 K1=.000000000594*EXP (6891.61/T) ! N2O4, CARTA
1230 K2=.0000000418*EXP (4869/T) ! N2O3, CARTA
1240 K3=.000000185*EXP (4723/T) ! HNO2, CARTA
1250 ! ////////////////////////////////////////////////////////////////////////
1260 REM REACTION CONSTANTS
1270 KNO=.221*EXP (1399/T) ! NO/O2; [1/atm-sec], INTEREL (BODENSTEIN)
1280 KEP=EXP (36.4-6900/T) ! NO/H2O2; [cm^3/gmol-s], BAVEJA
1290 KNO2=12.24 ! NO2/H2O2; [1/atm-sec], GRAY
1300 ! ////////////////////////////////////////////////////////////////////////
1310 REM N2O4 AND N2O3 ABSORPTION PARAMETERS (H*SQR(D*k)); [kmol/m^2-sec-atm]
1320 HDK1=10^(-.52-760/T) ! COUNCE EQUATION #46 (p.29)
1330 HDK2=.00159 ! SHERWOOD-PIGFORD-WILKE, p.360
1340 ! ////////////////////////////////////////////////////////////////////////
1350 REM CALCULATE TOWER PARAMETERS
1360 AE=.2204 ! TOWER AREA [Ft^2]
1370 A=AE*929 ! TOWER AREA; [Ft^2] TO [cm^2]
1380 Dt=6.357 ! TOWER DIAMETER [in]
1390 aE=108 ! PACKING SURFACE AREA [Ft^2/Ft^3]
1400 a=aE/30.48 ! PACKING AREA [cm^2/cm^3]
1410 NS=5/8 ! PACKING SIZE [in]
1420 Dp=NS*2.54 ! PACKING SIZE [cm]
1430 GV=V/A !  VAPOR RATE; [cm/s]
1440 REM CONVERT VOLUME RATE TO MOLAR RATE, ASSUME CONSTANT
1450 REM NEGLECT NOx CONTRIBUTION TO GAS VOLUME
1460 G=GV*(sqG/28.2) ! [gmol/s-cm^2]
1470 ! ////////////////////////////////////////////////////////////////////////
1480 REM CALCULATE PARTIAL PRESSURE INLET NOx; [atm]
1490 y=PPM/1000000
1500 NOc=p*y*PNO/100 ! CHEMICAL NO PARTIAL PRESSURE, INLET; [atm]
1510 NO2c=p*y*(1-PNO/100) ! CHEMICAL NO2 INLET PARTIAL PRESSURE; [atm]
1520 REM DEFINE OXYGEN PARTIAL PRESSURE, ASSUME CONSTANT
1530 O2=.21*p ! [atm], NOTE: DOES NOT ALLOW FOR COMBUSTION PROCESSES
1540 REM DEFINE H2O2 PARTIAL PRESSURE, ASSUME CONSTANT
1550 H2O2=PPER/100*(4/760)
1560 ! ////////////////////////////////////////////////////////////////////////
1570 DISP
1580 DISP "CALCULATE INLET NOx EQUILBRIUM"
1590 DISP
```

```
1600 LET NO=NOc @ NO2=NO2c
1610 NOx=NOc-NO2c
1620 GOSUB EQUIL  ! DEFINES INLET NOx CONSTITUENT LEVELS+++++++++++++++++++++++++
1630 ! ///////////////////////////////////////////////////////////////////////////
1640 REM DEFINE GAS CONSTANT
1650 GC=82.1 !  [atm-cm^3/gmol-K]
1660 GLC=.0821 ! [atm-m^3/kmol-K]
1670 GOSUB MASS  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
1680 REM DEFINE CONSTANT PORTIONS OF ABSORBTION EQUATIONS
1690 ACF=100*a*GLC*T*A*dh/V ! NOx ABSORBTION [atm-m^2-s/kmol]
1700 RCF=a*A*dh*.0001/Lm ! ACID FORMATION [s/m]
1710 ! ///////////////////////////////////////////////////////////////////////////
1720 DISP "CALCULATE CAUSTIC TOWER OUTPUT"
1730 DISP
1740 P(1)=N2O4
1750 P(2)=NO2
1760 P(3)=N2O3
1770 P(4)=HNO2
1780 P(5)=NO
1790 REM INITIALIZE ACID PRODUCTION TERMS
1800 AHNO2=0
1810 AHNO3=0
1820 FOR HT=1 TO 200
1830 LET n=HT
1840 GOSUB NaOH  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
1850 GOSUB EQUIL  ! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
1860 CPNOX(1,n)=NOx
1870 IF NOx<= ES THEN GOTO 1920 ! CHECK FOR EMISSION STANDARD SATISFACTION
1880 IF HT=1 THEN GOTO 1900
1890 IF ABS (LNOx-NOx)/LNOx<.00001 THEN GOTO 1920 ! MINIMUM REMOVAL CHECK
1900 LET LNOx=NOx ! SET COMPARISON TERM
1910 NEXT HT
1920 LET HCO=n*dh !   NaOH TOWER HEIGHT
1930 LET EXC=NOx
1940 CUI=(AHNO2+AHNO3)*Lm*3600*44*2.205 ! NaOH USAGE, [lb/Hr]
1950 PEC1=NOc ! SAVES NaOH TOWER EXHAUST CONCENTRATIONS
1960 PEC2=NO2c
1970 ! ///////////////////////////////////////////////////////////////////////////
1980 DISP "CALCULATE PEROXIDE TOWER OUTPUT"
1990 DISP
2000 REM RESET TO INLET CONDITIONS
2010 N2O4=P(1)
2020 NO2=P(2)
2030 N2O3=P(3)
2040 HNO2=P(4)
2050 NO=P(5)
2060 NOc=NO+N2O3+HNO2/2
2070 NO2c=NO2+2*N2O4+N2O3+HNO2/2
2080 NOx=NOc+NO2c
2090 REM INITALIZE ACID PRODUCTION TERMS
2100 LET AHNO2=0
2110 FOR CTS=1 TO 200
2120 LET n=CTS
2130 GOSUB H2O2  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2140 GOSUB EQUIL  ! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2150 CPNOX(2,n)=NOx
2160 IF NOx<= ES THEN 2210 ! CHECK FOR EMISSION STANDARD SATISFACTION
2170 IF CTS=1 THEN GOTO 2190
2180 IF ABS (LNOx-NOx)/LNOx<.00001 THEN GOTO 2210 ! MININUM REMOVAL CHECK
2190 LET LNOx=NOx ! SET COMPARISON TERM
```

```
2200 NEXT PTS
2210 HHP=n*dh ! PEROXIDE TOWER HEIGHT
2220 PTNOx=NOx
2230 PTNOc=NOc
2240 PTNO2c=NO2c
2250 GOSUB RUSAGE  ! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2260 ! /////////////////////////////////////////////////////////////////////////
2270 DISP "WATER ABSORBER CALCULATIONS"
2280 REM RESET TO INLET CONDITIONS
2290 N204=P(1)
2300 NO2=P(2)
2310 N203=P(3)
2320 HNO2=P(4)
2330 NO=P(5)
2340 NOc=NO+N203+HNO2/2
2350 NO2c=NO2+2*N204+N203+HNO2/2
2360 NOx=NOc+NO2c
2370 FOR WTS=1 TO 200
2380 LET n=WTS
2390 GOSUB WATER  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2400 GOSUB EQUIL  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2410 NEXT WTS
2420 GOSUB OPT  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2430 STOP
2440 ! --------------------------------------------------------------------------
2450 REM **REMAINDER OF PROGRAM IS SUBROUTINES**
2460 ! --------------------------------------------------------------------------
2470 ! //////////////////////////////////////////////////////////////////////////
2480 NaOH: ! *****************************************************************
2490 REM NaOH TOWER GAS/LIQUID EQUILBRIUM
2500 REM ROUTINE USES METRIC UNITS
2510 REM EQUATIONS ARE FROM LEVENSPIEL, COUNCE AND CARTA
2520 REM ABSORPTION FLUX (R TERMS) ARE IN [kmol/m^2-s]
2530 GOSUB NO2X  ! NO OXIDATION REACTION TO NO2 CALCULATION  ++++++++++++++++++
2540 RNO2=0 ! ASSUME NEGLIBLE
2550 RN204=N204*HDK1
2560 RN203=N203*HDK2
2570 RNO=0 ! ASSUME NEGLIBLE
2580 RHNO2=Kg*HNO2+DCHNO2*K3*NO*NO2*H2O/(T*GC*Kg)
2590 DNO2c=(RNO2+2*RN204+RN203+RHNO2/2)*ACF
2600 DNOc=(RNO+RN203+RHNO2/2)*ACF
2610 NO2c=NO2c-DNO2c+NO*NOOX
2620 NOc=NOc-DNOc-NO*NOOX
2630 NOx=NOc+NO2c
2640 AHNO2=AHNO2+RCF*(RNO2/2+RN204+2*RN203+RHNO2)
2650 AHNO3=AHNO3+RCF*(RNO2/2+RN204)
2660 RETURN
2670 ! //////////////////////////////////////////////////////////////////////////
2680 H2O2: ! ****************************************************************
2690 REM HYDROGEN PEROXIDE TOWER GAS/LIQUID EQUILBRIUM
2700 REM ROUTINE USES METRIC UNITS
2710 REM EQUATIONS ARE FROM LEVENSPIEL, SHERWOOD-PIGFORD-WILKE AND BAVEJA
2720 GOSUB NO2X  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
2730 RNO2=0 ! ASSUME NEGLIBLE
2740 RN204=N204*HDK1
2750 RN203=N203*HDK2
2760 NOS=NO*(CWP+CP)/NOVP
2770 RNO=SQR (DCNO*KEP)*SQR (CP)*NOS
2780 RHNO2=0
2790 NOc=NOc-(RNO+RN203+RHNO2/2)*ACF-NO*NOOX
```

```
2800 RR=H202/NO2
2810 TERM1=EXP ((KNO2*NO2*A*dh*(RR-1)/V)
2820 NO2OX=RR*(TERM1-1)/(RR*TERM1-1) ! NO2 CONVERSION WITH H202 (LEVENSPIEL)
2830 NO2c=NO2c-(RNO2+2*RN204+RN203+RHNO2/2)*ACF-NO2*NO2OX+NO*NOOX
2840 NOx=NOc+NO2c
2850 AH202(n)=NO2*NO2OX/2
2860 AHNO2=AHNO2+RCF*(RNO2/2+RN204+2*RN203+RHNO2+1.5*RNO/1000)
2870 RETURN
2880 ! //////////////////////////////////////////////////////////////////////
2890 EQUIL: ! **********************************************************
2900 REM ROUTINE ESTABLISHES NEW NOx GAS PHASE EQUILBRIUM FOR EACH INCREMENT
2910 REM ROUTINE USES METRIC UNITS
2920 REM OPTIMIZATION (MIN.) USING COMPLEX METHOD OF BOX
2930 JVAR=2 ! No. INDEPENDANT VARIABLES
2940 REM DEFINE N204 DISSOCIATION CONSTANT; SHERWOOD-PIGFORD-WILKE, p.348
2950 EA=1/SQR (1+4*K1*NO2c)
2960 RKL(2)=NO2c*2*EA/(1+EA) ! INITIAL NO2 VALUE (ESTIMATE)
2970 RKL(1)=NOc/(1+RKL(2)*K2) ! INITIAL NO VALUE (ESTIMATE)
2980 IF RKL(1)=0 THEN DX(1)=0 @ GOTO 3000
2990 DX(1)=10^(INT (LGT (RKL(1)))-1)
3000 IF RKL(2)=0 THEN DX(2)=0 @ GOTO 3020
3010 DX(2)=10^(INT (LGT (RKL(2)))-1)
3020 CPS=.000001 ! CONVERGENCE CRITERA
3030 ALP=3 ! EXPENSION COEFFICENT
3040 BETA=.5 ! CONTRACTION COEFFICENT
3050 NPTS=4 ! No. POINTS IN A COMPLEX
3060 MAXF=100000 ! Max. No. OF FUNCTION EVALUATIONS
3070 MAXSR=30 ! Max. No. OF CONTRACTIONS
3080 LET C=0 ! FUNCTION EVALUATION COUNTER
3090 FOR LE=1 TO JVAR
3100 RV(LE)=RKL(LE)
3110 NEXT LE
3120 GOSUB MODEL  ! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
3130 QDL=Q @ QDH=Q @ OB(1)=Q
3140 FOR J=1 TO JVAR
3150 RKK(1,J)=RKL(J)
3160 NEXT J
3170 NLOW=1 @ NHIGH=1
3180 FOR I=2 TO NPTS
3190 FOR K=1 TO JVAR
3200 AX=RND
3210 RT(K)=RKL(K)+DX(K)*(2*AX-1)
3220 IF RT(K)<0 THEN LET RT(K)=.00001
3230 RV(K)=RT(K)
3240 NEXT K
3250 GOSUB MODEL  ! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
3260 OB(I)=Q @ QD=Q
3270 FOR M=1 TO JVAR
3280 RKK(I,M)=RT(M)
3290 NEXT M
3300 IF QD>QDL THEN GOTO 3340
3310 QDL=QD
3320 NLOW=I
3330 GOTO 3370
3340 IF QD<QDH THEN GOTO 3370
3350 QDH=QD
3360 NHIGH=I
3370 NEXT I
3380 FOR N=1 TO JVAR
3390 AX=0
```

```
3400 FOR O=1 TO NPTS
3410 IF O=NHIGH THEN GOTO 3430
3420 AX=AX+RKK(O,N)
3430 NEXT O
3440 RC(N)=AX/(NPTS-1)
3450 NEXT N
3460 ALT=ALP
3470 NSR=0
3480 FOR PR=1 TO JVAR
3490 RT(PR)=ALT*(RC(PR)-RKK(NHIGH,PR))+RKK(NHIGH,PR)
3500 IF RT(PR)<0 THEN LET RT(PR)=(RKK(NHIGH,PR)+RKK(NLOW,PR))*.01
3510 RV(PR)=RT(PR)
3520 NEXT PR
3530 GOSUB MODEL  ! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
3540 QD=Q
3550 IF QD<QDH THEN GOTO 3590
3560 IF NSR>MAXSR THEN GOTO 3830
3570 ALT=BETA*ALT
3580 NSR=NSR+1 @ GOTO 3480
3590 OB(NHIGH)=QD
3600 C=C+1
3610 FOR S=1 TO JVAR
3620 RKK(NHIGH,S)=RT(S)
3630 NEXT S
3640 IF QD>QDL THEN GOTO 3670
3650 NLOW=NHIGH
3660 QDL=QD
3670 QDH=QDL
3680 FOR TE=1 TO NPTS
3690 IF OB(TE)<QDH THEN GOTO 3720
3700 QDH=OB(TE)
3710 NHIGH=TE
3720 NEXT TE
3730 IF (QDH+QDL)/(2*NOx)<CPS THEN GOTO 3860
3740 IF C<MAXF THEN GOTO 3380 ELSE GOTO 3830
3750 MODEL: ! ******************************************************************
3760 ROOTS=SQR (RV(1)*RV(2)*H2O*K3)
3770 Q1=NOc-(RV(1)+RV(1)*RV(2)*K2+ROOTS/2)
3780 Q2=NO2c-(RV(2)+2*RV(2)^2*K1+RV(1)*RV(2)*K2+ROOTS/2)
3790 IF RV(1)>NO OR RV(2)>NO2 THEN ADJ=100 ELSE ADJ=1 ! PENALITY FUNCTION
3800 Q=(ABS (Q1)+ABS (Q2))*ADJ
3810 RETURN
3820 REM NONCONVERGENCE RESET ROUTINE: EQUIL MUST CONVERGE ON NOx
3830 LET NPTS=5 ! INCREASE NUMBER OF POINTS IN A COMPLEX
3840 GOTO 3090
3850 REM EQUILBRIUM CONCENTRATION CALCULATIONS
3860 LET NO=RV(1)
3870 LET NO2=RV(2)
3880 N2O4=NO2^2*K1
3890 N2O3=NO*NO2*K2
3900 HNO2=SQR (NO*NO2*H2O*K3)
3910 NOc=NO+N2O3+HNO2/2
3920 NO2c=NO2+2*N2O4+N2O3+HNO2/2
3930 NOx=NOc+NO2c
3940 RETURN
3950 ! /////////////////////////////////////////////////////////////////////////
3960 OPT: ! ********************************************************************
3970 REM PROGRAM OUTPUT ROUTINE
3980 CLEAR
3990 PAGESIZE 24
```

```
4000 DISP
4010 DISP 'SYSTEM CHARACTERISTICS"
4020 DISP
4030 DISP "GAS FLOW=";VE;"Ft^3/min"
4040 DISP "LIQUID FLOW=";L;"gpm"
4050 DISP
4060 DISP "TOWER AREA=";AE;"Ft^2","          DIAMETER=";Dt/12;"Ft."
4070 DISP
4080 DISP USING 4090 ; "******************************************************"
4090 IMAGE 9X,54A
4100 DISP
4110 DISP "COLUMN CHARACTERISTICS"
4120 DISP
4130 DISP USING 4140 ; "INLET NOx","EXIT NOx","PACKING Ht.","REAGENT USED"
4140 IMAGE 13X,9A,5X,8A,5X,14A,5X,12A
4150 DISP USING 4160 ; "[ppm]","[ppm]","[Ft]","[lb/Hr]"
4160 IMAGE 15X,5A,8X,5A,9X,4A,15X,7A
4170 DISP
4180 DISP "PEROXIDE"
4190 DISP USING 4200 ; "TOWER",PPM,PTNOx*1000000/p,HHP*.03281,PER
4200 IMAGE 3X,5A,7X,5D,8X,5D,7X,4D.2D,13X,2D.2DE
4210 DISP
4220 DISP "CAUSTIC"
4230 DISP USING 4200 ; "TOWER",PPM,EXC*1000000/p,HCO*.03281,CUI
4240 DISP
4250 DISP "WATER"
4260 DISP USING 4200 ; "TOWER",PPM,NOx*1000000/p,WTS*dh*.03281,0
4270 PRINTER IS 601
4280 DUMP ALPHA 1,0
4290 BEEP
4300 DISP
4310 DISP "DONE"
4320 RETURN
4330 ! /////////////////////////////////////////////////////////////////////////
4340 UNITS: ! *****************************************************************
4350 REM CONVERTS ENGLISH AND METRIC UNITS TO THE OTHER
4360 V=VE*472 ! [ft^3/min] TO [cm^3/sec]
4370 L=VE/250*7.48 ! CALCULATES LIQUID RATE [gpm] BASED UPON GAS RATE (V/L=250)
4380 Lm=L*.0000631 ! [m^3/s]
4390 p=pT/760 ! [mmHg] TO [atm]
4400 T=(Tp-32)/1.8+273.15 ! [deg. F] TO [deg. K]
4410 REM CONVERT NOx STANDARD FROM ppm TO atm
4420 ES=NOXS/1000000*p
4430 REM CONVERT % SOLUTION INPUT TO [gmol/m^3]
4440 REM FIRST CALCULATE SOLUTION SPECFIC GRAVITY
4450 sqCS=2.13*PCAU/100+(1-PCAU/100) ! [g/cc]
4460 sqPS=1.438*PPER/100+(1-PPER/100) ! [g/cc]
4470 CC=PCAU/100*2.13*40/10^6 ! [gmol/cm^3]
4480 CW=(1-PCAU/100)*1*18/10^6 ! [gmol/cm^3]
4490 CP=PPER/100*1.438*34/10^6 ! [gmol/cm^3]
4500 CWP=(1-PPER/100)*1*18/10^6 ! [gmol/cm^3]
4510 REM CONVERT SPECFIC GRAVITY TO DENSITY
4520 sqG=pG*.01602 ! [g/cc]
4530 pL=7.48*8.32*sqCS ! [lb/ft^3]
4540 REM CALCULATE NO AND NO2 VAPOR PRESSURE via ANTOINE EQUATION
4550 NOVPE=940.5*EXP (8.142411-2374.39/(Tp+434.2)) ! [psia]
4560 NOVP=NOVPE*.06804 ! [atm]
4570 NO2VPE=1469.6*EXP (12.76017-1907.65/(Tp+616.0504)) ! [psia]
4580 NO2VP=NO2VPE*.06804 ! [atm]
4590 RETURN
```

```
4600 ! ////////////////////////////////////////////////////////////////////////
4610 DINPT: ! ******************************************************************
4620 REM DATA INPUT ROUTINE
4630 DISP "PROVIDE REQUESTED INPUTS ***CAUTION NOTE UNITS REQUESTED**"
4640 DISP
4650 DISP "SYSTEM GAS FLOW, [Ft^3/min]; EXIT GAS VELOCITY (STACK); [ft/min]";
4660 INPUT VE,GDV
4670 DISP
4680 DISP "NOx CONCENTRATION [ppm] AND % NO IN THE NOx";
4690 INPUT PPM,PNO
4700 DISP
4710 DISP "INLET GAS CONDITIONS, TEMP. [F], PRESS. [mmHg], DENSITY [lb/Ft^3]";
4720 INPUT Tp,pT,pG
4730 DISP
4740 DISP "WATER PARAMETERS, VISCOSITY [cp] AND VAPOR PRESSURE [atm]";
4750 INPUT uL,H2O
4760 DISP
4770 DISP "REAGENT STRENGTHS, SODIUM HYDROXIDE AND HYDROGEN PEROXIDE [wt.%]";
4780 INPUT PCAU,PPER
4790 CLEAR
4800 DISP USING "8/,28X,15A" ; "PROGRAM RUNNING"
4810 RETURN
4820 ! ////////////////////////////////////////////////////////////////////////
4830 MASS: ! ****************************************************************
4840 REM GAS PHASE MASS TRANSFER COEFFICENT CALCULATION FOR HNO2
4850 REM ASSUMES VALUES CONSTANT DUE TO DILUTE SYSTEM
4860 REM ALSO ASSUMES IDEAL GAS BEHEAVIOR
4870 REM CALCULATION FROM ONDA, J. Chem. Japan, 1968
4880 LET VISG=.0001812 ! [g/cm-sec] ASSUMES 68 F; ERROR 3% at +- 20 F
4890 REM GAS VISCOSITY FROM PERRY'S 6th TABLE 3-311
4900 REM FOLLOWING ARE DIFFUSION COEFFICENTS; [cm^2/sec] (**ASSUMED CONSTANT**)
4910 DCHNO2=.00014*(uL^(-1.1))*((GC*T/HNO2)^(-.6)) ! HNO2, equ 2.29 S-P-W
4920 DCNO=.000028807 ! NO, BRAVJA
4930 TRM1=(G/(a*VISG))^.7
4940 TRM3=(a*Dp)^(-2)
4950 TRM2=(VISG/(pG*DCHNO2))^(1/3)
4960 TRM4=a*DCHNO2/(GC*T)
4970 Kg=5.23*TRM1*TRM2*TRM3*TRM4 ! [gmol/cm^2-sec-atm]
4980 RETURN
4990 ! ////////////////////////////////////////////////////////////////////////
5000 EMCONC: ! EMISSION STANDARD ROUTINE***************************************
5010 SDIA=VE/GDV*12 ! [in] STACK DIAMETER
5020 NOXS=2400/SDIA ! [ppm] EXHAUST CRITERA BASED ON VISABILITY STND. FOR NO2
5030 IF NOXS>200 THEN LET NOXS=200 ! SETS MAX. PERMISSABLE EXIT CONCENTRATION
5040 RETURN
5050 ! ////////////////////////////////////////////////////////////////////////
5060 RUSAGE: ! H2O2 USAGE ROUTINE*********************************************
5070 REM ACCOUNTS FOR H2O2 USED WITH NO, NO2 AND HNO2 (TO HNO3)
5080 LET SAH2O2=0
5090 FOR PUPT=1 TO n
5100 SAH2O2=SAH2O2+AH2O2(PUPT)
5110 NEXT PUPT
5120 PER=SAH2O2*V/(GC*T)*269.9+AHNO2*Lm*(60)*2.205*34 ! [lb/Hr]
5130 RETURN
5140 ! ////////////////////////////////////////////////////////////////////////
5150 NO2X: ! NO/O2 REACTION TO NO2, EQUATION PER COUNCE APPENDIX B  ***********
5160 M=-(NO/(2*O2))
5170 TERMA=NO*O2*A*dh*KNO/V
5180 TERMB=(LOG (1+M)*M/(1+M)+1)/(1+M)
5190 REM INTERVAL HALVING ROUTINE TO SOLVE FOR REACTION CONVERSION
```

```
5200 LET XNO(1)=.02 @ XNO(2)=.01
5210 FOR XR=1 TO 30
5220 TERMV=(LOG ((1+M*XNO(XR))/(1-XNO(XR)))+M/(1+M)+1/(1-XNO(XR))) [illegible]
5230 XFN(XR)=TERMA-(TERMV-TERMB)
5240 IF ABS (XFN(XR))<.00000001 THEN GOTO 5320
5250 IF XR=1 THEN GOTO 5310
5260 IF XFN(XR)<0 EXOR XFN(XR-1)<0 THEN GOTO 5290
5270 IF XNO(XR)<XNO(XR-1) THEN DH=-1 ELSE DH=1
5280 GOTO 5300
5290 IF XNO(XR)<XNO(XR-1) THEN DH=1 ELSE DH=-1
5300 XNO(XR+1)=XNO(XR)+DH*ABS ((XNO(XR)-XNO(XR-1))/2)
5310 NEXT XR
5320 NOOX=XNO(XR)
5330 RETURN
5340 ! //////////////////////////////////////////////////////////////////////////
5350 WATER: ! WATER ABSORPTION SUBROUTINE ***************************************
5360 RN204=N204*HDK1
5370 RN203=N203*HDK2
5380 GOSUB NO2X  ! +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
5390 NOc=NOc-ACF*RN203-NO*NOOX
5400 NO2c=NO2c-ACF*(RN204+RN203)+NO*NOOX
5410 NOx=NOc+NO2c
5420 RETURN
5430 ! //////////////////////////////////////////////////////////////////////////
5440 END
```

VITA

Tracy J. Coates was born on November 4, 1955 in San Diego, California. He attended elementary schools in California graduating from Simi Valley High School in June 1973. In September of that year he entered the University of Virginia from which he received the degree of Bachelor of Science in Chemical Engineering in May 1977.

In June 1977 he began work with Virginia Chemicals in Portsmouth, Virginia as a Process Engineer continuing with them until April 1981. From March 1981 to August 1985 he then held a project engineering position with Nuclear Fuel Services, Inc. in Erwin, Tennessee leaving that firm to work as an Applications Engineer for Texas Instruments in Johnson City, Tennessee in September 1985.

In September 1983 he entered The Graduate School of the University of Tennessee, Knoxville as a evening student at the Kingsport, Tennessee Graduate Center. He received the Master of Science in Chemical Engineering degree in December 1986.

He is a member of the American Institute of Chemical Engineers, the National Society of Professional Engineers and is a Registered Professional Engineer (Chemical) in Tennessee and Virginia. After graduation Mr. Coates will continue his employment with Texas Instruments.