Scrubbing of Gaseous Nitrogen Oxides in Packed Towers

Nitrogen oxide removal efficiencies of up to 97% were obtained in tests using columns packed with Intalox saddles. These studies were conducted at atmospheric pressure with water as the scrub solution and nitrogen oxide feed concentrations of up to 10%. A mathematical model based on mass-transfer, kinetic, and equilibrium data is presented; calculated removal efficiencies using this model agree very well with the experimental data.

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SCOPE

Experiments were conducted to evaluate the aqueous absorption of NO_x at atmospheric pressure and 298 K in towers packed with 6- and 13-mm Intalox saddles. The feed NO_x partial pressure was varied from 0.01 to 0.10 atm; the scrub liquor was usually water. A mathematical model for the process was developed and tested against the experimental results.

The absorption of NO_x into aqueous media is important in pollution abatement, as well as in the production of nitric acid. There is an enormous amount of piecewise literature, of both a fundamental and an applied nature, on this subject. However, an integrated understanding of the basic mechanisms involved in this process has not previously been available.

Perhaps the first noteworthy attempt to combine both chemical reaction rate and equilibrium information and mass transfer data into a mathematical model for NO_x absorption was that of Andrews and Hanson (1961). Their model agrees well with data from their single sieve-plate column. Andrews and Hanson (1961) provided for the absorption of N_2O_4, NO_2, HNO_3, HNO_2, and N_2O_3 by utilizing fixed overall stoichiometry to predict the absorption-desorption associated with the scrubbing of NO_x. This model was adapted for use in packed towers (Hoftyzer and Kwanten 1972) and is reported to work with fair success in predicting the NO_x removal efficiency in high-pressure absorbers. However, the fixed overall stoichiometry of these absorption models represents only a limiting situation. Recent studies by Makhotkin and Shamsutdinov (1976), Counce and Perona (1979), and Koegler (1979), as well as some earlier observations by Andrews and Hanson (1961) and Koval and Peters (1960), have shown that aqueous HNO_3 scrubber solutions have a steady-state capacity for retaining considerable concentrations of HNO_2. The overall stoichiometry of some sparged, semibatch NO_2 absorption studies by Makhotkin and Shamsutdinov (1976) was found to be

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

only when a steady-state concentration of aqueous HNO_2 was present. During the period of time before steady state was reached, the molar ratio of the production of gaseous NO to the NO_2 absorbed was less than the 1:3 ratio expected from Eq. 1. In multistage NO_x scrubbing studies with a recirculating liquid phase, Counce and Perona (1979), as well as Koegler (1979), noticed a similar effect. Counce and Perona (1980) developed a mechanistic model for NO_x removal in their sieve-plate column that takes into account the described buildup of HNO_2 on the overall scrubbing process; this model fitted their data fairly closely during this transient before steady state and at steady state. From these studies, it can be seen that the buildup of aqueous HNO_2 coincides with a loss in NO_x scrubbing efficiency, which can be attributed to a loss in the liquid capacitance to retain NO in the liquid phase. This phenomenon was also noted by Andrews and Hanson (1961), who considered only the steady-state NO_x absorption performance of their system. This type of steady-state performance is not generally a good assumption for packed NO_x absorbers in which the HNO_2 liquid phase concentration varies significantly along the tower.

The scrubbing of NO_x compounds in packed towers with nonrecycle of the scrubber liquid will almost certainly be in the transition region, with respect to the establishment of a steady-state aqueous HNO_2 concentration, for at least part of the tower. This hypothesis is based on the observed capacity of aqueous solutions for retaining HNO_2 and the low liquid holdup times in packed towers. It seems logical to describe the NO_x absorption mechanisms of the liquid phase and the gas phase in dynamic terms. The overall column performance will then be a function of total system dynamics, without the restriction of assumed stoichiometric constraints.

CONCLUSIONS AND SIGNIFICANCE

Nitrogen oxide removal efficiencies of 55–97% were obtained over a wide range of experimental conditions. A mathematical model was developed that was based on mass-transfer information for packed towers and chemical reaction kinetics of the NO_x-HNO_x-H_2O system. Predictions using this model agree with the experimental results quite well. This mathematical model will be useful for NO_x scrubber design and other process simulation activities. Extension of this model for use at lower temperatures and higher nitric acid strengths requires additional data and careful quantification of the reverse rates of the N_2O_3

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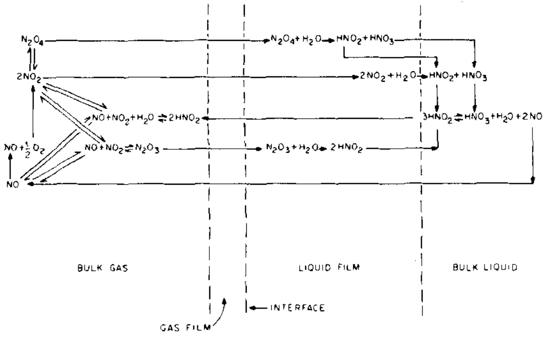

Figure 1. Model for describing mass-transfer and chemical-reaction phenomena.

and N_2O_4 hydrolysis reactions. The depletion of nitrous acid in packed towers under similar conditions to those described here is treated separately by Counce (paper in preparation). More extensive reviews on the aqueous scrubbing of NO_x have been presented by Hoftyzer and Kwanten (1972), Sherwood et al. (1975), and Counce (1980).

THEORY

A scheme for describing mass-transfer and chemical-reaction phenomena for the NO_x-HNO_x-H_2O system is given in Figure 1. This scheme is quite similar to one used previously by Hoftyzer and Kwanten (1972), who illustrated all the conceivable transfer and reaction routes involved in NO_x scrubbing. The present model, as diagramed in Figure 1, allows for calculations in the bulk-gas phase, within the gas and liquid films, and the bulk-liquid phase. The gas phase is assumed to be saturated with H_2O (taking into consideration the temperature and the liquid HNO_3 concentration). The partial pressure of HNO_3 is usually small over solutions of low acid molarity compared with the NO_x partial pressures in these experiments and was taken to be zero. The indicated gaseous chemical equilibria were assumed to apply at all times in the gas phase. The predicted HNO_2 partial pressure is usually small compared with the H_2O partial pressure and is always assumed to be equal to or below the saturation partial pressure. The model accommodates the oxidation of gaseous NO to NO_2 in the bulk-gas phase.

The steady-state transport of component i across both the gas and liquid films is expressed by Counce (1980) as

$$\bar{R}_i = -k_{G,i}\frac{dP_i}{d\zeta} = (Ek_L)_i(C_i^* - C_i), \qquad (2)$$

utilizing a dimensionless film thickness ζ.

In the case of physical absorption or desorption, the enhancement factor E is taken to be unity. The absorbing species are NO_2, N_2O_4, and N_2O_3. From the work of Corriveau (1971), Denbigh and Prince (1947), Koval and Peters (1960), and Peters and Koval (1959), it may be concluded that HNO_2 is not an absorbing species although it cannot be ruled out as a desorbing species. The other desorbing species is NO, which is formed from the bulk-liquid-phase decomposition of HNO_2.

The absorption-desorption phenomena involved in the scrubbing of nitrogen oxides from gas streams have been simulated for an incremental column volume. The height of this incremental section is small so that average component partial pressures and concentrations, as well as gas and liquid flow rates in the increment, may be used in rate equations for interphase transport. The gas phase is assumed to be ideal, and isothermal conditions are further assumed to prevail. The model computes the partial pressure of gas species leaving the increment and the concentrations of liquid species entering the increment. This requires known or assumed information about the gas and liquid streams entering and leaving the increment respectively.

The nitrogen oxide species of importance in the gas phase are NO, NO_2, N_2O_3, N_2O_4, and HNO_2. The partial pressures of "chemical" nitrogen dioxide and nitric oxide are defined as

$$P_{NO_2^*} = P_{NO_2} + 2P_{N_2O_4} + P_{N_2O_3} + \frac{1}{2}P_{HNO_2} \qquad (3)$$

and

$$P_{NO^*} = P_{NO} + P_{N_2O_3} + \frac{1}{2}P_{HNO_2} \qquad (4)$$

Another quantity ξ is the difference in the NO_2^* and NO^* species, and this partial pressure difference is represented by

$$\xi = P_{NO_2^*} - P_{NO^{\cdot}} = P_{NO_2} + 2P_{N_2O_4} - P_{NO} \qquad (5)$$

The bulk-gas-phase component partial pressures of these species are calculated using existing equilibrium information as

$$P_{N_2O_4} = K_1P_{NO_2}^2, \qquad (6)$$

$$P_{N_2O_3} = K_2P_{NO}P_{NO_2} \qquad (7)$$

and

$$P_{HNO_2} = (K_3P_{H_2O}P_{NO}P_{NO_2})^{1/2} \qquad (8)$$

These gas-phase equilibrium expressions are assumed to apply throughout the gas phase. The NO_x component partial pressures are calculated from known partial pressures of NO_2^* and NO^*.

The steady-state gas-phase performance equation for the incremental absorption-desorption-reaction of NO_2^* and NO^* may be expressed as

$$\text{input} = \text{output} \pm \begin{array}{c}\text{disappearance or}\\ \text{appearance due to}\\ \text{gas-phase reaction}\end{array} \pm \begin{array}{l}\text{disappearance or}\\ \text{appearance due to}\\ \text{absorption or}\\ \quad\text{desorption}\end{array} \qquad (9)$$

In the previous equation, the disappearance terms are positive while the appearance terms are negative. The molar input of the ith species to the column increment may be represented as $G(P_i)_{in}/(RT)$ while the output is $G(P_i)_{out}/(RT)$.

The extent of the gas-phase oxidation of NO to NO_2 occurring in the increment X_{NO} is computed and used to adjust the molar rates of NO and NO_2; this leaves the increment as $\pm GP_{NO}X_{NO}/(RT)$. The term X_{NO} is the conversion of NO to NO_2. The molar rate of O_2 leaving the increment is also corrected. The equation used in the calculation of X_{NO} is given by Counce (1980) for plug flow conditions as

$$\frac{k_5(P_{NO})_{in}(P_{O_2})_{in}\Delta V}{G} - \frac{1}{1+b'}\left(\frac{1}{1-X_{NO}} + \frac{b'}{1+b'}\ln\frac{1+b'X_{NO}}{1-X_{NO}}\right) = 0 \qquad (10)$$

The disappearance and/or appearance phenomena of NO_2^* and NO^* in the gas phase due to absorption and desorption may be simplified by defining an absorption flux for each gaseous NO_x component in terms of gas-phase and enhanced liquid-phase mass-transfer coefficients and partial pressure and concentration driving forces, Eq. 2:

$$\bar{R}_i = -k_{G,i}\frac{dP_i}{d\zeta} = (Ek_L)_i(C_i^* - C_i)$$

Thus, desorption is inverse absorption. The desorbing species are HNO_2 and NO. The reaction that produces NO is considered to be sufficiently slow that it does not affect the concentration profile in the liquid phase; thus, the enhancement factor E is unity for both of these cases. The molar rate of disappearance or appearance of NO_2^* and NO^* in the incremental gas phase is obtained as $\bar{R}_{NO_2^*}a\Delta V$ and $\bar{R}_{NO^*}a\Delta V$. The fluxes of NO_2^* and NO^* and their difference ξ are found as

$$\bar{R}_{NO_2^*} = \bar{R}_{NO_2} + 2\bar{R}_{N_2O_4} + \bar{R}_{N_2O_3} + \frac{1}{2}\bar{R}_{HNO_2}, \qquad (11)$$

$$\overline{R}_{NO^*} = \overline{R}_{N_2O_3} + \frac{1}{2}\overline{R}_{HNO_2} + \overline{R}_{NO}, \tag{12}$$

and

$$\overline{R}_\xi = \overline{R}_{NO_2} + 2R_{N_2O_4} - \overline{R}_{NO} \tag{13}$$

(note that the flux of HNO_2 will be restricted to desorption only).

The total flux of NO_x is

$$\overline{R}_{NO_x} = \overline{R}_{NO_2^*} + \overline{R}_{NO^*} \tag{14}$$

Representing the NO_2^* and NO^* fluxes in terms of a pressure gradient across a dimensionless film thickness,

$$R_{NO_2^*} = -k_{G,NO_2^*}\frac{dP_{NO_2^*}}{d\zeta}, \tag{15}$$

and

$$\overline{R}_{NO^*} = -k_{G,NO^*}\frac{dP_{NO^*}}{d\zeta} \tag{16}$$

Utilizing Eqs. 3 and 4 and the differentiation of Eqs. 6–8, the gradients of N_2O_4, N_2O_3, and HNO_2 in the gas film may be expressed in terms of NO and NO_2 as

$$\frac{dP_{N_2O_4}}{d\zeta} = 2K_1P_{NO_2}\frac{dP_{NO_2}}{d\zeta}, \tag{17}$$

$$\frac{dP_{N_2O_3}}{d\zeta} = K_2P_{NO}\frac{dP_{NO_2}}{d\zeta} + K_2P_{NO_2}\frac{dP_{NO}}{d\zeta}, \tag{18}$$

and

$$\frac{dP_{HNO_2}}{d\zeta} = \frac{1}{2}\left(K_3P_{H_2O}\frac{P_{NO}}{P_{NO_2}}\right)^{1/2}\frac{dP_{NO_2}}{d\zeta} + \frac{1}{2}\left(K_3P_{H_2O}\frac{P_{NO_2}}{P_{NO}}\right)^{1/2}\frac{dP_{NO}}{d\zeta} \tag{19}$$

The fluxes of NO_2^* and NO^* through the gas film are calculated using appropriate gas-phase mass-transfer coefficients as

$$\begin{aligned}-\overline{R}_{NO_2^*} = {} & \left[k_{G,NO_2} + 4k_{G,N_2O_4}K_1P_{NO_2} + k_{G,N_2O_3}K_2P_{NO} + \frac{1}{4}k_{G,HNO_2}\left(\frac{K_3P_{H_2O}P_{NO}}{P_{NO_2}}\right)^{1/2}\right]\frac{dP_{NO_2}}{d\zeta} \\ & + \left[k_{G,N_2O_3}K_2P_{NO_2} + \frac{1}{4}k_{G,HNO_2}\left(\frac{K_3P_{H_2O}P_{NO_2}}{P_{NO}}\right)^{1/2}\right]\frac{dP_{NO}}{d\zeta},\end{aligned} \tag{20}$$

$$\begin{aligned}-\overline{R}_{NO^*} = {} & \left[k_{G,N_2O_3}K_2P_{NO} + \frac{1}{4}k_{G,HNO_2}\left(\frac{K_3P_{H_2O}P_{NO}}{P_{NO_2}}\right)^{1/2}\right]\frac{dP_{NO_2}}{d\zeta} \\ & + \left[k_{G,N_2O_3}K_2P_{NO_2} + \frac{1}{4}k_{G,HNO_2}\left(\frac{K_3P_{H_2O}P_{NO_2}}{P_{NO}}\right)^{1/2} + k_{G,NO}\right]\frac{dP_{NO}}{d\zeta}\end{aligned} \tag{21}$$

and

$$-\overline{R}_\xi = (k_{G,NO_2} + 4k_{G,N_2O_4}K_1P_{NO_2})\frac{dP_{NO_2}}{d\zeta} - (k_{G,NO})\frac{dP_{NO}}{d\zeta} \tag{22}$$

The absorption-desorption of the indicated gas species through the liquid film is represented by

$$\begin{aligned}\overline{R}_{NO_2^*} = {} & \left(\frac{k_L}{H}\right)_{NO_2}P^*_{NO_2} + 2\left(\frac{\sqrt{Dk}}{H}\right)_{N_2O_4}P^*_{N_2O_4} + \left(\frac{\sqrt{Dk}}{H}\right)_{N_2O_3}P^*_{N_2O_3} \\ & + \frac{1}{2}\left(\frac{k_L}{H}\right)_{HNO_2}P^*_{HNO_2} - \frac{1}{2}k_{L,HNO_2}C_{HNO_2},\end{aligned} \tag{23}$$

$$\begin{aligned}\overline{R}_{NO^*} = {} & \left(\frac{\sqrt{Dk}}{H}\right)_{N_2O_3}P^*_{N_2O_3} + \frac{1}{2}\left(\frac{k_L}{H}\right)_{HNO_2}P^*_{HNO_2} \\ & - \frac{1}{2}k_{L,HNO_2}C_{HNO_2} + \left(\frac{k_L}{H}\right)_{NO}P^*_{NO} - k_{L,NO}C_{NO},\end{aligned} \tag{24}$$

and

$$\overline{R}_\xi = \left(\frac{k_L}{H}\right)_{NO_2}P^*_{NO_2} + 2\left(\frac{\sqrt{Dk}}{H}\right)_{N_2O_4}P^*_{N_2O_4} - \left(\frac{k_L}{H}\right)_{NO}P^*_{NO} + k_{L,NO}C_{NO} \tag{25}$$

assuming that the hydrolysis of N_2O_3 and N_2O_4 are fast and of first order and that Henry's law applies at the gas-liquid interface.

Separating the variables in Eq. 22 and preparing for integration yields

$$-\overline{R}_\xi\int_0^\zeta d\zeta = k_{G,NO_2}\int_{P_{NO_2}}^{P^*_{NO_2}}dP_{NO_2} + 4k_{G,N_2O_4}K_1 \times \int_{P_{NO_2}}^{P^*_{NO_2}}P_{NO_2}dP_{NO_2} - k_{G,NO}\int_{P_{NO}}^{P^*_{NO}}dP_{NO} \tag{26}$$

Integration of the above equation and substitution of $\overline{R}_\xi$ for the liquid phase (Eq. 25) yields, after some rearrangement,

$$P^*_{NO} = \frac{\alpha_1P^*_{NO_2} + \alpha_2(P^*_{NO_2})^2 - \alpha_3P_{NO_2} - \alpha_4P^2_{NO_2} + \alpha_5P_{NO} + \alpha_6C_{NO}}{\alpha_5 + \alpha_7}, \tag{27}$$

Rearranging Eq. 21 and substituting for Eq. 20 yields

$$\frac{dP_{NO_2}}{d\zeta} = \frac{\alpha_8(R_{NO_2^*}) + \alpha_9(\overline{R}_{NO^*})}{\alpha_{10}\alpha_8 - \alpha_{11}\alpha_{12}}, \tag{28}$$

where $\overline{R}_{NO_2^*}$ and $\overline{R}_{NO^*}$ are defined in Eqs. 23 and 24. The individual component fluxes may now be calculated in terms of bulk and interfacial values of NO and NO_2.

Rewriting the gas-phase performance equation specifically for NO_2^* and NO^* and rearranging allows the calculation of the partial pressures of the NO_2^* and NO^* leaving the increment

$$(P_{NO_2^*})_{out} = (P_{NO_2^*})_{in} - \left(\overline{R}_{NO_2} + 2\overline{R}_{N_2O_4} + \overline{R}_{N_2O_3} + \frac{1}{2}\overline{R}_{HNO_2}\right)\left(\frac{a\Delta VRT}{G}\right) + P_{NO}X_{NO} \tag{29}$$

and

$$(P_{NO^*})_{out} = (P_{NO^*})_{in} - \left(\overline{R}_{N_2O_3} + \frac{1}{2}\overline{R}_{HNO_2} + \overline{R}_{NO}\right)\left(\frac{a\Delta VRT}{G}\right) - P_{NO}X_{NO} \tag{30}$$

In terms of total NO_x partial pressure,

$$(P_{NO_x})_{out} = (P_{NO_2^*})_{out} + (P_{NO^*})_{out} \tag{31}$$

Further adjustments of the gas flow rate and component partial pressures due to bulk-gas component removal or addition are made before beginning the next incremental calculation.

In the liquid phase, the absorption reactions produce aqueous nitric and nitrous acids. Nitric acid is relatively stable in the liquid phase and has a fairly low vapor pressure at ambient conditions. Aqueous nitrous acid is unstable at ambient conditions and has a substantial vapor pressure. Overall steady-state performance equations for the liquid phase of the incremental absorption-desorption-reaction with respect to aqueous HNO_2 and HNO_3 may be expressed as

$$\begin{array}{l}\text{input of}\\ \text{HNO}_3\end{array} = \begin{array}{l}\text{output of}\\ \text{HNO}_3\end{array} - \begin{array}{l}\text{production from}\\ \text{reactions of}\\ \text{absorbing NO}_x\\ \text{components}\end{array} - \begin{array}{l}\text{production from}\\ \text{liquid-phase}\\ \text{decomposition}\\ \text{of HNO}_2\end{array} \tag{32}$$

and

$$\begin{array}{l}\text{input of}\\ \text{HNO}_2\end{array} = \begin{array}{l}\text{output of}\\ \text{HNO}_2\end{array} - \begin{array}{l}\text{appearance as}\\ \text{product from}\\ \text{reactions of}\\ \text{absorbing NO}_x\\ \text{components}\end{array} + \begin{array}{l}\text{decomposition}\\ \text{of HNO}_2\text{ in}\\ \text{liquid phase}\\ \text{and physical}\\ \text{desorption}\\ \text{of HNO}_2\end{array} \tag{33}$$

The molar inputs of nitric and nitrous acids are $L(C_{HNO_3})_{in}$ and $L(C_{HNO_2})_{in}$ whereas the outputs are $L(C_{HNO_3})_{out}$ and $L(C_{HNO_2})_{out}$.

The rate of acid production in the liquid phase (as well as the possible removal in the case of nitrous acid) due to the absorption flux of NO_x species from the gas phase is

$$\sum_{i=1}^{n} \psi_i \overline{R}_i a \Delta V$$

The term ψ_i is a stoichiometric factor. These production rates for nitric acid and nitrous acid are

$$\sum_{i-1}^{n} \psi_i \overline{R}_i a \Delta V = \left(\frac{1}{2}\overline{R}_{NO_2} + \overline{R}_{N_2O_4}\right) a \Delta V \qquad (34)$$

and

$$\sum_{i=1}^{n} \psi_i \overline{R}_i a \Delta V = \left(\frac{1}{2}\overline{R}_{NO_2} + \overline{R}_{N_2O_4} + 2\overline{R}_{N_2O_3} + \overline{R}_{HNO_2}\right) a \Delta V \qquad (35)$$

The equilibrium as expressed in

$$3HNO_2(1) \leftrightarrow H^+(1) + NO_3^-(1) + H_2O(1) + 2NO(1) \qquad (36)$$

is assumed to apply in the liquid phase from the work of Abel and Schmid (1928a, 1929). This equilibrium reaction proceeds to the right as NO desorbs from the aqueous phase. The absorption of NO is neglected due to its low solubility. The bulk-phase concentration of NO is calculated from a modified Abel-Schmid equilibrium expression

$$C_{NO} = \left(\frac{a^3_{HNO_2}}{H^2_{NO} K_6 a_{H^+} a_{NO_3^-}}\right)^{1/2} \qquad (37)$$

Thus, the production of nitric acid in the increment due to the decomposition may be represented by $1/2k_{L,NO}(C_{NO} - C^*_{NO})$ and the disappearance of nitrous acid by $-3/2k_{L,NO}(C_{NO} - C^*_{NO})$. Incorporating these relationships into the liquid-phase performance equation yields, after rearrangement,

$$(C_{HNO_3})_{in} = (C_{HNO_3})_{out} - \left(\frac{1}{2}\overline{R}_{NO_2} + \overline{R}_{N_2O_4} - \frac{1}{2}\overline{R}_{NO}\right)\frac{a\Delta V}{L} \qquad (38)$$

and

$$(C_{HNO_2})_{in} = (C_{HNO_2})_{out} - \left(\frac{1}{2}\overline{R}_{NO_2} + \overline{R}_{N_2O_4} + 2\overline{R}_{N_2O_3} + \overline{R}_{HNO_2} + \frac{3}{2}\overline{R}_{NO}\right)\frac{a\Delta V}{L} \qquad (39)$$

By knowing or assuming $(P_{NO_2^*})_{in}$, $(P_{NO^*})_{in}$, $(C_{HNO_2})_{out}$, and $(C_{HNO_3})_{out}$, one may calculate similar quantities at the top of the increment provided $\overline{R}_i$ in the liquid phase may be calculated for the individual NO_x species. The calculation of these individual flux equations was previously shown. The desorptive flux of NO was shown by Abel and Schmid (1928a,b,c) to be limited by the decomposition reaction of HNO_2 occurring in the bulk liquid; this flux was found always to be less than the theoretical maximum predicted by Komiyama and Inoue (1978) and Counce (paper in preparation).

EXPERIMENTAL APPARATUS AND PROCEDURE

Two packed columns were used with inside diameters of 0.076 and 0.102 m. These columns were packed with ceramic Intalox saddles with diameters of 6 and 13 mm, respectively. Several depths of packing were used in these studies. Other equipment was associated with the scrubber-liquid supply, metering, and sampling systems and the gaseous supply, metering, and sampling systems. The liquid was distributed in the tower approximately 0.03 m above the top of the packing.

In the 0.076-diam. column, the gas was entered into the packing through the packing support; however, the gas was injected directly into the bottom of the packing in the 0.102-m diam. column. Both feed and effluent liquid streams were manually sampled.

Carrier gases of air on N_2 were metered by rotameter to either of the two packed towers; NO_2^* or NO^*/NO_2^* feed mixtures were produced by blending in the correct portions of these gases. Steam could also be added to this feed gas. The gas stream leaving the packed tower was cooled and demisted for entrained acid recovery and for control of the water content. The volume of this recovered liquid and the acid content were determined; the acid from this step was always less than 1% of the NO_x input. A nitric acid bubble column on the effluent gas stream provided the upstream pressure necessary to route a stream through the gas analysis equipment. Thus, the scrubber column was operated slightly above atmosphere pressure.

All streams entering and leaving the experimental column were analyzed for gaseous nitrogen oxides or their aqueous reaction products. Infrared detectors for gaseous NO and NO_2 were operated under such temperature and moisture conditions that essentially all of the +II and +IV valent oxides were in the NO and NO_2 state for analysis; this analysis compared very favorably with standard wet chemistry analysis techniques. The NO_x content of a gas stream was calculated as the total of the NO^* and NO_2^* concentration. The NO^* to NO_2^* ratio of the feed was determined when needed by obtaining the previously mentioned NO and NO_2 analyses using a nitrogen (nonoxidizing) carrier gas; this type of analysis was necessary, as the NO^* to NO_2^* ratio of commercially-obtained N_2O_3 changes slowly as NO preferentially evaporates from the solution. The acidity of the liquid feed stream was checked to verify its purity. Separate samples from the effluent liquid stream were stabilized immediately with the addition of hydrogen peroxide and ceric sulfate for later analysis of total nitrous acid content. The raw data consisted of the mole fractions of NO_x in the feed and effluent gas streams, the ratio of NO^* to NO_2^* in the feed gas; the acidity of the feed and effluent liquid streams, gas and liquid flow rates, temperatures and pressures, and the volume and acidity of liquid removed in the mist removal step. This data is presented by Counce (1980). The entire experimental setup was located in a fume hood.

RESULTS

A screening series of tests was initially conducted to get a broad understanding of NO_x absorption in packed towers. The response variable is the NO_x conversion X_{NO_x}. This series of tests is presented in Table 1. The effect of variable i on the NO_x conversion is defined by

$$\text{effect of variable } i = \frac{\sum[(X_{NO_x}\text{ at high values of } i - X_{NO_x}\text{ at low values of } i)]}{\text{half the number of factorial runs}} \qquad (40)$$

TABLE 1. DATA FOR SATURATED FRACTIONAL FACTORIAL DESIGN FOR STUDYING SEVEN NO_x SCRUBBING VARIABLES IN EIGHT RUNS

Variables	−(Low)	+(High)
1. Scrubber liquid flow rate ($m^3 \cdot s^{-1}$)	3.50×10^{-5}	5.25×10^{-5}
2. Scrubber liquid HNO_3 molarity ($kmol \cdot m^{-3}$)	0	3.0
3. Partial pressure of NO_x in feed gas (atm)	0.05	0.20
4. Steam flow rate in feed gas ($kg \cdot s^{-1}$)	0	5.0×10^{-4}
5. Air or nitrogen as diluent gas	Nitrogen	Air
6. Scrubber liquid temperature (K)	286	306
7. Oxidation state of NO_x in feed gas	0.5	1.0

	Variable							Overall NO_x Conversion
Run	1	2	3	4	5	6	7	X_{NO_x}
A	−	−	−	−	+	−	−	69
B	+	−	−	+	−	−	+	86
C	−	+	−	+	+	+	+	91
D	+	+	−	−	−	+	−	52
E	−	−	+	−	−	+	+	90
F	+	−	+	+	+	+	−	78
G	−	+	+	+	−	−	−	82
H	+	+	+	−	+	−	+	96
Effect	−4.9	−0.6	11.8	7.6	6.4	−5.6	20.6	

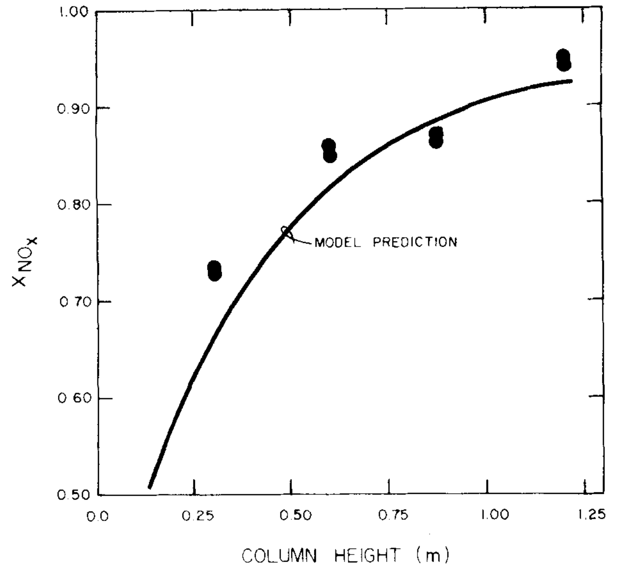

Figure 2. Experimental and model predicted NO_x conversions at varying column heights; the other parameters were: $G = 1.5 \times 10^{-3}$ std $m^3 \cdot s^{-1}$; $L = 3.5 \times 10^{-5}$ $m^3 \cdot s^{-1}$; $Y_{NO_x,in} = 0.05$; and $P_T = 1.1$ atm.

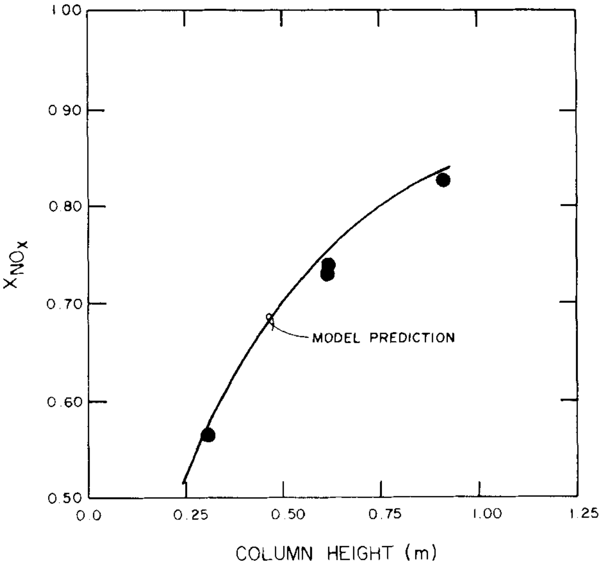

Figure 4. Experimental and model predicted NO_x conversions at varying column heights, the other parameters were: $G = 3.2 \times 10^{-3}$ std $m^3 \cdot s^{-1}$; $L = 5.0 \times 10^{-5}$ $m^3 \cdot s^{-1}$; $Y_{NO_x,in} = 0.05$; and $P_T = 1.1$ atm.

The most pronounced effect on the NO_x conversion was produced by variation in the oxidation state of the gas. This is a well-known phenomenon in NO_x scrubbing; in general, the NO* species have a much lower solubility and reactivity than the NO$_2^*$ species. The second largest effect was produced by the variation in the partial pressure of NO_x in the feed gas; this might be explained by the higher NO_x partial pressure producing a larger proportional amount of the higher molecular weight species, which are more absorbable and reactive. The increase in removal efficiency with the addition of steam to the feed gas was previously noted by Counce and Perona (1979). The increase in removal efficiency with air instead of nitrogen can be attributed to the oxidation of the NO* species to the NO$_2^*$ state, which increases the solubility and reactivity of these species. The decrease in removal efficiency with increased temperature can be credited to the decrease in higher molecular weight species, such as N_2O_4 and N_2O_3, due to the nature of the gas-phase equilibrium reactions. The decrease in scrubber efficiency with increased gas rate may be attributed to the loss of residence time in the column. The liquid rate apparently had an inverse effect in these studies; this probably indicates some overriding second-order effects because the gas-liquid interfacial area and the liquid-phase mass-transfer coefficient are known to increase with the liquid rate. These studies were useful in deciding the level of complexity required in a mathematical explanation of this system.

A series of experiments using the 0.102-m diam. tower packed with 13-mm Intalox saddles provide the basis for the model development. Most of these runs were conducted at NO_x partial pressures of approximately 0.05 and 0.01 atm. The model development consisted of determining the value of $(\sqrt{Dk}/H)_{N_2O_4}$ that allowed the model prediction to represent the data most accurately. The value of $(\sqrt{Dk}/H)_{N_2O_3}$, obtained by Corriveau (1971), is the only such constant known. The effect of the ionic strength on these constants should be minimal as these studies were conducted using a water/dilute-acid scrub solution. The values of K_1, K_2, and K_3 were obtained from the works of Verhoek and Daniels (1931), Beattie and Bell (1957), and Wayne and Yost (1951), respectively. The use of these constants maintained consistency as they have been

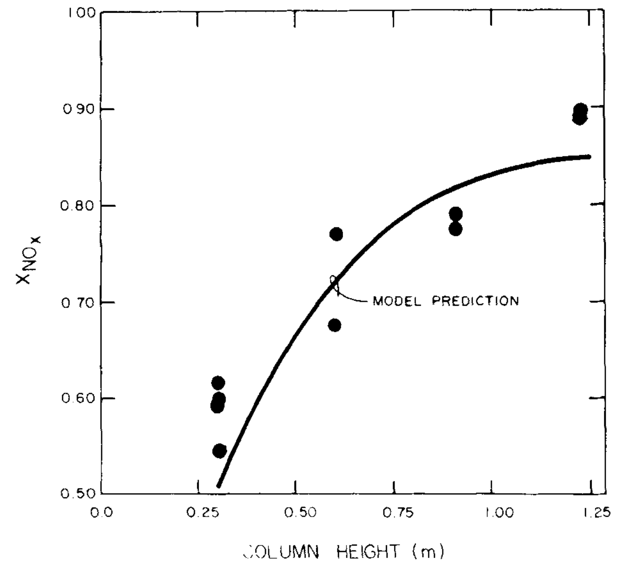

Figure 3. Experimental and model predicted NO_x conversions at varying column heights, the other parameters were: $G = 3.2 \times 10^{-3}$ std $m^3 \cdot s^{-1}$; $L = 3.5 \times 10^{-5}$ $m^3 \cdot s^{-1}$; $Y_{NO_x,in} = 0.05$; and $P_T = 1.1$ atm.

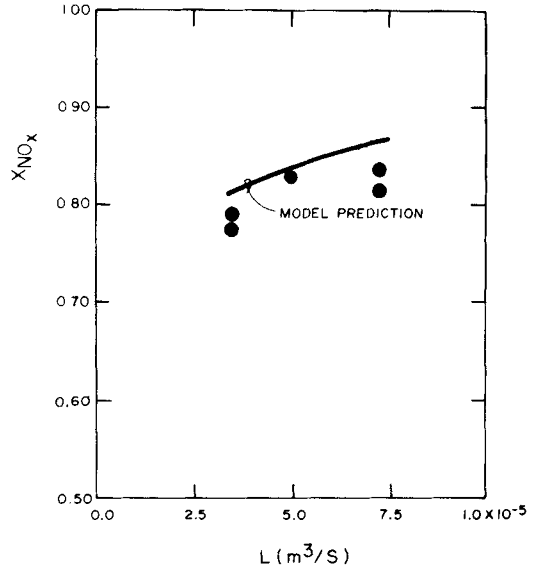

Figure 5. Experimental and model predicted NO_x conversions at varying liquid rates, the other parameters were: $G = 3.2 \times 10^{-3}$ std $m^3 \cdot s^{-1}$; $h = 0.90$ m; $Y_{NO_x,in} = 0.05$; and $P_T = 1.1$ atm.

TABLE 2. THE EXPERIMENTAL AND MODEL[a] PREDICTED CONVERSION OF NO_x FOR A FEED GAS CONTAINING NO^* AND NO_2^*

Run	X_{NO_x} Experimental	X_{NO_x} Calculated
10-29	0.648	0.544
10-30	0.821	0.737
10-31	0.779	0.693

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[a] Model prediction is based on $(\sqrt{Dk}/H)_{N_2O_4} = 11.0 \times 10^{-5}$.

used in the calculations of $(\sqrt{Dk}/H)_{N_2O_4}$ and $(\sqrt{Dk}H)_{N_2O_3}$. The Henry's Law constant for NO in water is from Loomas (1928); similar constants for NO_2 and HNO_2 are from recommendations by Schwartz and White (1981) respectively. The rate constant for the oxidation of NO used in these calculations was that of Bodenstein (1918). The value of K_6 was from the work of Abel and Schmid (1928c). The values of k_G were calculated from a correlation by Onda et al. (1968). The constant 5.23 was used with this correlation instead of 2.00, which is normally used for Raschig rings and Berl saddles that are smaller than 15 mm. The values of a and k_L were taken from experimental results using the 13-mm Intalox saddles (Danckwerts 1970) and calculated for the 6-mm Intalox saddles using equations from Puranik and Vogelpohl (1974) and from Mohunta et al. (1969). These selections are consistent with recent reviews in these areas by Laurent and Charpentier (1974) and by Sherwood et al. (1975). The correlations for effective interfacial areas and liquid-phase mass-transfer coefficients are the only such correlations known that include data from the tests using Intalox saddles. The most critical coefficient is the value of $(\sqrt{Dk}/H_{N_2O_4})$. These values range from 5.7×10^{-4} to 11×10^{-4} kmol·atm^{-1}·m^{-2}·s^{-1}. (See Corriveau 1971 and Dekker et al., 1959, respectively.) Most of the NO_x absorption efficiency data are bounded by computations using the model previously presented and by the above values of $(\sqrt{Dk}/H)_{N_2O_4}$. Model predictions of X_{NO_x} using the value of $(\sqrt{Dk}/H)_{N_2O_4}$ (Dekker et al., 1959) gave excellent agreement with the experimental data.

The N_2O_4 absorption route accounted for more than 99% of the predicted NO_x absorption for the runs with a fully oxidized feed gas of ~0.05 atm. This is in contrast with predictions at NO_2^* and NO^* partial pressures of 0.002 and 0.008 atm where the N_2O_4 route accounted for ~50% of NO_x absorption with the N_2O_3 route accounted for ~48%; the remaining NO_x removal predicted in these runs resulted from the absorption of NO_2.

Data for experiments conducted using the 0.102-m diam. column and a fully oxidized feed gas are shown in Figures 2 through 5. These plots include calculated NO_x conversions using the $(\sqrt{Dk}/H)_{N_2O_4}$ values of Dekker et al. (1959).

The data for runs with a partially oxidized feed gas, along with the model predictions, are presented in Table 2. In this comparison, the model prediction is consistently lower than the experimentally observed values of X_{NO_x}.

A series of four runs was conducted using the 0.102-m diam. column at NO_x feed partial pressures of about 0.01 atm. A summary of the run conditions and model predictions is presented in Table 3. A comparison between the model predicted and the experimental X_{NO_x} shows good agreement.

TABLE 3. EXPERIMENTAL AND CALCULATED RESULTS[a] FOR RUNS WITH THE NO_x FEED PARTIAL PRESSURE AT ABOUT 0.01 ATM

Variables	−(Low)	+(High)
1. Gas rate (m^3·s^{-1})	~3×10^{-3}	~5×10^{-3}
2. Liquid rate (m^3·s^{-1})	~1.8×10^{-5}	~3.6×10^{-5}
3. Percent of NO_x with N in +IV state	~20	~100

Run	Variable 1	2	3	$(X_{NO_x})_{exp}$	$(X_{NO_x})_{cal}$
10-32-2F	−	+	+	0.64	0.61
10-32-2G	−	−	−	0.10	0.06
10-32-2H	+	+	−	0.00	0.06
10-32-2I	+	−	+	0.48	0.43

Calculated X_{NO_x} is based on $(\sqrt{Dk}/H)_{N_2O_4}$ of 11.0×10^{-5}.

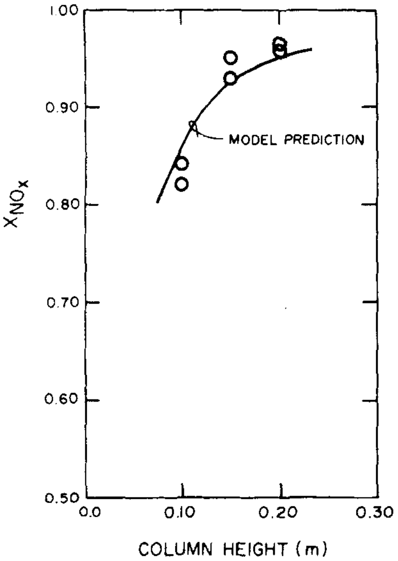

Figure 6. Experimental and model predicted conversions at varying column heights, the other parameters were: $G = 3.3 \times 10^{-4}$ std m^3·s^{-1}; $L = 4.5 \times 10^{-5}$ m^3·s^{-1}; $Y_{NO_x,in} = 0.10$; and $P_T = 1.1$ atm.

Additional data were taken using the 0.074-m diam. column. Some selected experimental conversions from these data are compared with calculated values and presented in Figure 6. Again, reasonable agreement with the previous selection of the $(\sqrt{Dk}/H)_{N_2O_4}$ value is observed.

Other experimental activities concerned the depletion of nitrous acid from solutions in contact with nitrogen (Counce, paper in preparation). In depletion studies conducted using the smaller diameter tower at fairly low gas-rate to liquid-rate ratios, the depletion processes seem well described by the Abel-Schmid (1928a) stoichiometry. (See Eq. 36.) In depletion studies conducted using the larger diameter column at much higher gas-rate to liquid-rate ratios, the depletion processes apparently involve both the decomposition, described by Abel and Schmid (1928a), and the physical desorption of HNO_2 (Counce, 1980).

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NOTATION

a = gas-liquid interfacial area (m^{-1})
a_i = activity of ith specie (kmol·m^{-3})
b' = $-P_{NO}/2P_{O_2}$
C_i = bulk-liquid concentration of component i (kmol·m^{-3})
C_i^* = interfacial concentration of component i (kmol·m^{-3})
d = differential operator
D = diffusivity (m^2·s^{-1})
E_i = enhancement factor, the factor by which the absorption of component i is increased by liquid reaction
(g) = gas
G = volumetric gas flow rate (m^3·s^{-1})
h = height of packing
H = Henry's Law constant (m^3 atm·kmol^{-1})

HNO_x = $HNO_2 + HNO_3$
in = in
k = a first-order or a pseudo-first-order rate constant (s^{-1})
k_5 = a third-order reaction rate constant for the oxidation of gaseous NO
K_1 = an equilibrium constant defined by $P_{N_2O_4}/P^2_{NO_2}$ (atm^{-1})
K_2 = an equilibrium constant defined by $P_{N_2O_3}/P_{NO}P_{NO_2}$ (atm^{-1})
K_3 = an equilibrium constant defined by $P^2_{HNO_2}/P_{NO}P_{NO_2}P_{H_2O}$ (atm^{-1})
K_6 = an equilibrium constant defined by $C_{H^+}\,C_{NO_3^-}C^2_{NO}/C^3_{HNO_2}$ ($kmol \cdot m^{-3}$)
k_G = gas-phase mass-transfer coefficient ($kmol \cdot m^{-2} \cdot atm^{-1} \cdot s^{-1}$)
$k_{G,i}$ = gas-phase mass-transfer coefficient for component i ($kmol \cdot m^{-2} \cdot atm^{-1} \cdot s^{-1}$)
k_L = liquid-phase mass-transfer coefficient ($m \cdot s^{-1}$)
$k_{L,i}$ = liquid-phase mass-transfer coefficient for component i ($m \cdot s^{-1}$)
ln = base e logarithmic function
L = liquid flow rate ($m^3 \cdot s^{-1}$)
(l) = liquid
NO^* = $NO + N_2O_3 + 1/2HNO_2$
NO_2^* = $NO_2 + 2N_2O_4 + N_2O_3 + 1/2HNO_2$
NO_x = $NO^* + NO_2^*$
out = out
P_i = bulk-gas partial pressure of component i (atm)
P_i^* = interfacial partial pressure of component i (atm)
P_T = total pressure (atm)
r_i = reaction rate for component i ($kmol \cdot m^{-3} \cdot s^{-1}$ or $atm \cdot s^{-1}$)
R = gas law constant ($m^3\ atm \cdot kmol^{-1} \cdot K^{-1}$)
$\bar{R}_i$ = absorption rate for component i ($kmol \cdot m^{-2} \cdot s^{-1}$)
V = column volume (m^3)
X_i = fractional conversion of component i; i.e., $X_{NO_x} = [(P_{NO_x})_{in} - (P_{NO_x})_{out}]/[(P_{NO_x})_{in} + \epsilon(P_{NO_x})_{out}]$
Y_i = mole fraction of component i
α_1 = $k_{G,NO_2} + (k_L/H)_{NO_2}$
α_2 = $2k_{G,N_2O_4} K_1 + 2(\sqrt{Dk}/H)_{N_2O_4}K_1$
α_3 = k_{G,NO_2}
α_4 = $2k_{G,N_2O_4}K_1$
α_5 = $k_{G,NO}$
α_6 = $k_{L,NO}$
α_7 = $k_{L,NO}/H_{NO}$
α_8 = $k_{G,N_2O_3}K_2P_{NO_2} + \frac{1}{4}k_{G,HNO_2}(K_3P_{H_2O}P_{NO_2}/P_{NO})^{1/2} + k_{G,NO}$
α_9 = $k_{G,N_2O_3}K_2P_{NO_2} + \frac{1}{4}k_{G,HNO_2}(K_3P_{H_2O}P_{NO}/P_{NO_2})^{1/2}$
α_{10} = $k_{G,NO_2} + 4k_{G,N_2O_4}K_1P_{NO_2} + k_{G,N_2O_3}K_2P_{NO} + \frac{1}{4}k_{G,HNO_2}(K_3P_{H_2O}P_{NO}/P_{NO_2})^{1/2}$
α_{11} = $k_{G,N_2O_3}P_{NO_2} + \frac{1}{4}k_{G,HNO_2}(K_3P_{H_2O}P_{NO_2}/P_{NO})^{1/2}$
α_{12} = $k_{G,N_2O_3}K_2P_{NO} + \frac{1}{4}k_{G,HNO_2}(K_3P_{H_2O}P_{NO}/P_{NO_2})^{1/2}$
ΔV = incremental column volume (m^3)
Δ = signifies a difference in the final and initial values
ζ = dimensionless film thickness
ρ_G = density of gas ($kmol \cdot m^{-3}$)
ρ_L = density of liquid ($kmol \cdot m^{-3}$)
ψ_i = stoichiometric factor
ξ = $P_{NO_2^*} - P_{NO^*}$
ϵ = fractional volumetric change due to bulk removal of gas components

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