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## SCRUBBING OF NITROGEN OXIDES WITH NITRIC ACID SOLUTIONS

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A mathematical model is developed for an equilibrium stage analysis of nitrogen oxides absorption in nitric acid solutions. Using equilibrium data available from the literature, the model demonstrates that 15-35 wt% nitric acid may be efficiently used to reduce pollutant emissions in  $\text{NO}_x$ -containing gases having low degree of oxidation. Lower oxides of nitrogen accumulate in the liquid as nitrous acid which is carried away by the nitric acid solution. The scrubbed gas contains a reduced concentration of nitrogen oxides and has a higher degree of oxidation than the feed gas.

KEYWORDS Scrubbing  $\text{NO}_x$  Nitric acid  $\text{NO}$  oxidation.

### INTRODUCTION

Nitrogen oxides removal from gaseous streams is required in many industrial operations. Because of their harmful effect on the ecosystem an almost complete  $\text{NO}_x$  removal must be accomplished in many cases.

Generally speaking two types of technologies exist for abatement of nitrogen oxides emissions: (i) dry processes and (ii) wet processes. Dry processes include adsorption and catalytic reduction. The latter ones rely on the introduction of a reducing agent (typically  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$  or  $\text{CO}$ ) to reduce nitrogen oxides to  $\text{N}_2\text{O}$  or  $\text{N}_2$ . These processes tend to be cost inefficient due to their nonregenerative nature. Wet processes, on the other hand, employ liquid absorbents to scrub nitrogen oxides. Water scrubbing tends to be very inefficient being strongly limited by the relatively inert nature of nitric oxide. Since in many  $\text{NO}_x$  pollution control problems  $\text{NO}$  comprises the major fraction of the total  $\text{NO}_x$  content, it is necessary to use chemically reactive scrubbing solutions. Hydrogen peroxide solutions and  $\text{Fe}^{++}$  solutions are examples of possible scrubbing agents. The first however lead to non-regenerable processes and the second to low capacity and to loss of reactant due to the relative instability when in contact with  $\text{O}_2$ -containing gases.

The difficulties due to the very low reactivity and solubility of  $\text{NO}$  may be overcome by converting it in the gas phase to more reactive nitrogen oxides prior to wet scrubbing. Ozone and  $\text{ClO}_2$  are efficient oxidizing agents but are expensive and may introduce waste disposal problems.  $\text{NO}$  can be oxidized by oxygen in the gas phase. The homogeneous reaction is, however, a slow termolecular process

whose rate becomes extremely low at low NO partial pressures. Furthermore its overall activation energy is negative so that an increase in temperature does not lead in general to an increased rate of oxidation (Bodenstein, 1922). In the range of NO<sub>x</sub> partial pressures encountered in pollution control, prohibitively large residence times are normally required to achieve appreciable NO conversion.

Selective catalytic oxidation of NO with oxygen has been demonstrated. Karlsson and Rosemberg (1984) have recently reviewed literature on the subject and performed a thorough experimental investigation on the performance of a variety of catalysts. Typically, the catalysts investigated exhibited optimum performance at about 200°F, while providing 50–70% NO conversion at practical space velocities. Catalyst deactivation was, however, evident after a relatively short period of time.

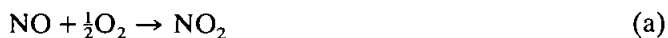
An alternative to the gas phase oxidation of NO is the use of nitric acid solutions as oxidizing–scrubbing agents (Bolme, 1977; Bolme and Horton, 1979). In this process NO<sub>x</sub>—containing gases with low degrees of nitrogen oxidation (i.e. containing predominantly NO) are contacted countercurrently with a nitric acid solution of appropriate strength. NO is oxidized by HNO<sub>3</sub> in aqueous solution, forming nitrous acid which in turn is carried away by the scrubbing liquid. The HNO<sub>2</sub>-laden liquid is regenerated by removing HNO<sub>2</sub> in a stripping unit operated at high temperature or by oxidizing it to HNO<sub>3</sub> with oxygen. When the nitric acid strength is chosen appropriately, the gas exiting from the scrubbing column has a reduced NO<sub>x</sub> concentration and an increased degree of nitrogen oxidation. Thus, final washing with alkali may efficiently remove nitrogen oxides completely via the absorption of higher oxides of nitrogen such as N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>. The process, which appears to be optimally suited for tail gas NO<sub>x</sub> emission control from nitric acid plants, has the fundamental advantage of solvent regenerability and efficiency. Furthermore it permits recovery of the scrubbed nitrogen oxides in useful concentrated form. In a nitric acid plant these gases may be sent to the main absorption tower for HNO<sub>3</sub> production, thereby reducing the loss of fixed nitrogen in the process.

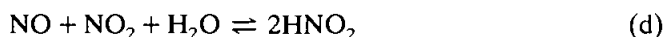
In this paper an equilibrium-stage model for NO<sub>x</sub> scrubbing with aqueous nitric acid is presented. The model is based solely on available equilibrium data and accounts for the complex chemistry of the nitrogen oxides system. Numerical solution of the model demonstrates the principle of the operation allowing analysis and evaluation in comparison with existing pollution control techniques.

## CHEMISTRY OF THE OXIDATION–ABSORPTION PROCESS

Of the various forms of nitrogen oxides, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, HNO<sub>2</sub> and HNO<sub>3</sub> are predominant under typical process conditions.

The following reactions occur in the gas phase

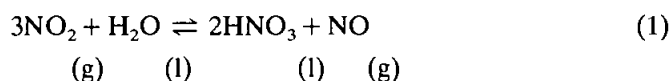




Reaction (a) is essentially irreversible at low temperature. Its rate is extremely small in the range of partial pressures encountered in pollution control. Thus, unless extremely large reactor volumes are considered, its effects are relatively unimportant and will be neglected in the following development. It should be noted, however, that any NO oxidation will in any case be beneficial to NO<sub>x</sub> removal processes.

The equilibrium constants of reactions (b) to (e) are available in the literature. Extensive reviews have been given by Sherwood *et al.* (1975), Lefers (1980), and Schwartz and White (1981). A list of selected values has been given by Carta (1984). Reactions (b) to (e) are known to be rather fast under typical process conditions, although only scattered kinetic data exist.

The reactions of nitrogen oxides in aqueous solutions are considerably more complex, involving also several ionic species such as NO<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and H<sup>+</sup>. A considerable amount of experimental work has been published regarding the equilibrium in the heterogeneous system NO<sub>x</sub>-HNO<sub>x</sub>-H<sub>2</sub>O. Chemical equilibrium in terms of the partial pressures of NO and NO<sub>2</sub> and the weight fraction of HNO<sub>3</sub> in solution has been determined by Abel and Schmid (1928), Chambers and Sherwood (1937), Epshtein (1939), and Denbigh and Prince (1947). An overall heterogeneous reaction is normally written as



and the equilibrium is empirically expressed by

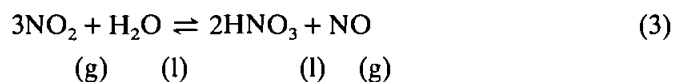
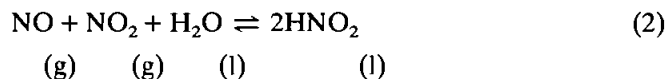
$$K = \frac{P_{\text{NO}}}{P_{\text{NO}_2}^3}$$

$$K' = \frac{P_{\text{NO}}}{P_{\text{N}_2\text{O}_4}^{3/2}}$$

In these equations both  $K$  and  $K'$  are functions of the acid strength (Sherwood *et al.*, 1975). Carberry (1959) has shown that  $K'$  is very nearly independent of temperature. It should be noted that these expressions for the heterogeneous equilibrium constant do not account explicitly for the effects of dissolved HNO<sub>2</sub> on the equilibrium. These effects are of course important in the NO oxidation-absorption process with nitric acid and cannot be neglected. In this case in fact, HNO<sub>2</sub> is the main reaction product and may limit the equilibrium absorption of nitrogen oxides. The above equations may nevertheless be used for the analysis of nitric acid manufacturing columns since in this case HNO<sub>2</sub> tends to reach a constant steady concentration after just a few stages. The effects of HNO<sub>2</sub> are in this case built in the numerical values of  $K$  or  $K'$ .

Theobald (1968) has provided experimental equilibrium data that permit evaluation of the effects of dissolved HNO<sub>2</sub>. Carta and Pigford (1983) have

correlated Theobald's data in terms of the two independent reactions



by defining the empirical equilibrium constants

$$K_2 = \frac{W_{\text{HNO}_2}^2}{P_{\text{NO}} \cdot P_{\text{NO}_2}} \quad (4)$$

$$K_3 = \frac{W_{\text{HNO}_3}^2 P_{\text{NO}}}{P_{\text{NO}_2}^3} \quad (5)$$

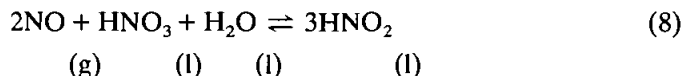
where  $K_2$  and  $K_3$  are functions of the nitric acid weight fraction,  $W_{\text{HNO}_3}$

$$\ln K_2 = A_2 - B_2 W_{\text{HNO}_3} \quad (6)$$

$$\ln K_3 = A_3 - B_3 W_{\text{HNO}_3} \quad (7)$$

Numerical values for the constants in Eqs. (6) and (7) are given in Table I.  $W_{\text{HNO}_2}$  has virtually no effect on  $K_2$  and  $K_3$  owing to its low value. As shown by Longstaff and Singer (1954)  $\text{N}_2\text{O}_4$  is essentially absent from nitric acid solutions below a nitric acid concentration of about 40 wt%.

By combining reactions 2 and 3 one obtains



which shows how  $\text{HNO}_2$  can be formed from the oxidation of NO with nitric acid in aqueous solution. Experimental investigations on the kinetics of reaction 8 in concentrated nitric acid solutions (10–35 wt%) have been conducted by Lewis and Edgar (1911), Schmid and Bahr (1964), Schmid and Krichel (1964), and by Carta and Pigford (1983). The stoichiometry of reaction (8) was confirmed, but the reaction was found to follow an autocatalytic kinetics and was zero-order in NO. The reaction rate increased sharply with nitric acid concentration.

Analysis of the thermodynamic problem of the  $\text{NO}_x$ – $\text{HNO}_x$ – $\text{H}_2\text{O}$  equilibrium reveals that an additional equilibrium relationship is needed to relate the partial

TABLE I  
Constants for Eqs. (6) and (7)

$T(^{\circ}\text{C})$	$A_2$	$B_2$	$A_3$	$B_3$
25	–1.074	6.632	17.498	26.055
35	–2.230	5.951	15.634	24.998
45	–3.229	5.324	14.379	24.697

pressure of water to its concentration in the liquid. This would normally be obtained by equating the fugacities of H<sub>2</sub>O in the gas and in the liquid phase. However, due to the highly non ideal liquid behavior the following correlation based on vapor pressure data of Taylor (1925) may be used to estimate the partial pressure of water over nitric acid solutions at 25°C

$$p_{\text{H}_2\text{O}} = 3.03 \times 10^{-2} - 7.35 \times 10^{-4} W_{\text{HNO}_3} - 9.25 \times 10^{-2} W_{\text{HNO}_3}^2 + 6.29 \times 10^{-2} W_{\text{HNO}_3}^3 \quad (9)$$

This equation provides values of  $p_{\text{H}_2\text{O}}$  in atm in excellent agreement with those given by Davis and DeBruin (1964). Analogous correlations may be developed at different temperatures.

### EQUILIBRIUM STAGE MODEL

In order to assess the operability of nitric oxide oxidation-absorption with nitric acid it is necessary to develop a model that adequately reflects the complex chemistry of the nitrogen oxides-water system. Without loss of generality the following assumptions will be made. HNO<sub>3</sub>, HNO<sub>2</sub> and H<sub>2</sub>O are considered to be the only species present in appreciable concentration in the liquid phase. Reactions (b) to (e) are assumed to occur in the gas phase which in turn is assumed to behave ideally. Reaction (a) is neglected owing to its modest importance at low NO<sub>x</sub> partial pressures and because doing so will set a lower limit to the process efficiency. Equations (4), (5) and (9) are used to relate the partial pressures of NO, NO<sub>2</sub> and H<sub>2</sub>O to the weight fractions of HNO<sub>2</sub>, HNO<sub>3</sub> and H<sub>2</sub>O in the liquid.

The scrubbing column is assumed to consist of a countercurrent cascade of well mixed reactors in each of which chemical equilibrium is achieved. Because of the low nitrogen oxides concentrations used, the column is assumed to be isothermal.

With reference to Figure 1 the following material balances on N, H, O and inert may be written for each equilibrium stage  $i$

$$\begin{aligned} G_{i+1} \{ Y_{\text{NO}} + Y_{\text{NO}_2} + 2Y_{\text{N}_2\text{O}_3} + 2Y_{\text{N}_2\text{O}_4} + Y_{\text{HNO}_2} + Y_{\text{HNO}_3} \}_{i+1} \\ - G_i \{ Y_{\text{NO}} + Y_{\text{NO}_2} + 2Y_{\text{N}_2\text{O}_3} + 2Y_{\text{N}_2\text{O}_4} + Y_{\text{HNO}_2} + Y_{\text{HNO}_3} \}_i \\ + L_{i-1} \left\{ \frac{W_{\text{HNO}_2}}{M_{\text{HNO}_2}} + \frac{W_{\text{HNO}_3}}{M_{\text{HNO}_3}} \right\}_{i-1} - L_i \left\{ \frac{W_{\text{HNO}_2}}{M_{\text{HNO}_2}} + \frac{W_{\text{HNO}_3}}{M_{\text{HNO}_3}} \right\}_i = 0 \quad (10) \end{aligned}$$

$$\begin{aligned} G_{i+1} \{ Y_{\text{HNO}_2} + Y_{\text{HNO}_3} + 2Y_{\text{H}_2\text{O}} \}_{i+1} - G_i \{ Y_{\text{HNO}_2} + Y_{\text{HNO}_3} + 2Y_{\text{H}_2\text{O}} \}_i \\ + L_{i-1} \left\{ \frac{W_{\text{HNO}_2}}{M_{\text{HNO}_2}} + \frac{W_{\text{HNO}_3}}{M_{\text{HNO}_3}} + 2 \frac{W_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \right\}_{i-1} \\ - L_i \left\{ \frac{W_{\text{HNO}_2}}{M_{\text{HNO}_2}} + \frac{W_{\text{HNO}_3}}{M_{\text{HNO}_3}} + 2 \frac{W_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \right\}_i = 0 \quad (11) \end{aligned}$$

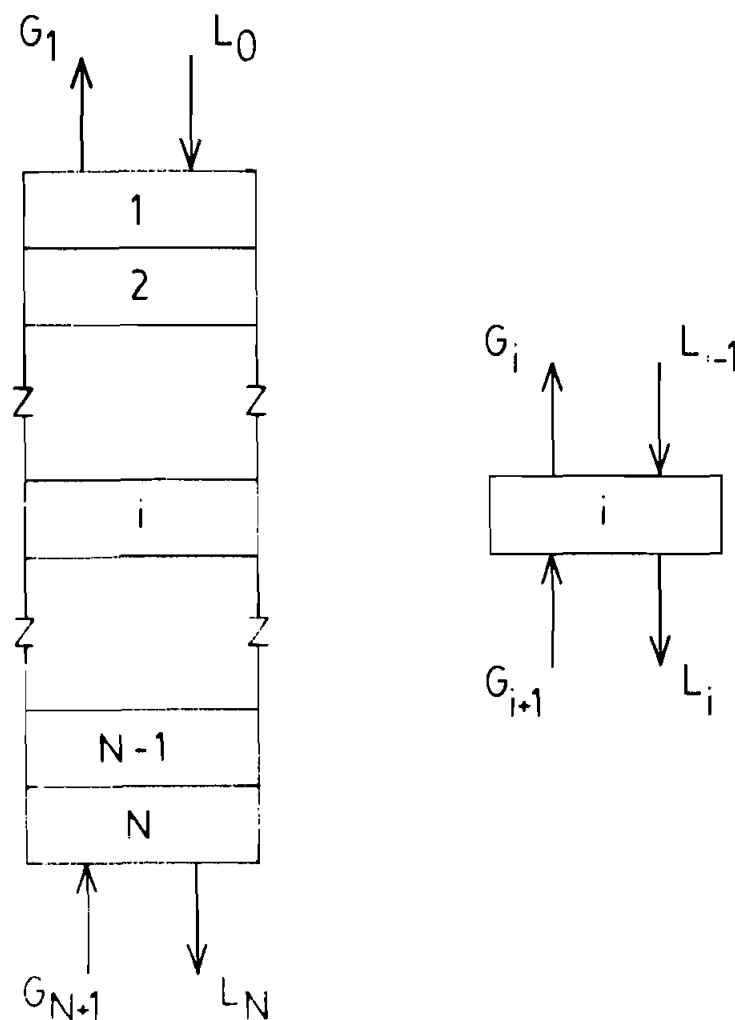


FIGURE 1 Sketch of equilibrium stage model.

$$\begin{aligned}
 & G_{i+1} \{ Y_{\text{NO}} + 2Y_{\text{NO}_2} + 3Y_{\text{N}_2\text{O}_3} + 4Y_{\text{N}_2\text{O}_4} + 2Y_{\text{HNO}_2} + 3Y_{\text{HNO}_3} + Y_{\text{H}_2\text{O}} \}_{i+1} \\
 & - G_i \{ Y_{\text{NO}} + 2Y_{\text{NO}_2} + 3Y_{\text{N}_2\text{O}_3} + 4Y_{\text{N}_2\text{O}_4} + 2Y_{\text{HNO}_2} + 3Y_{\text{HNO}_3} + Y_{\text{H}_2\text{O}} \}_i \\
 & + L_{i-1} \left\{ 2 \frac{W_{\text{HNO}_2}}{M_{\text{HNO}_2}} + 3 \frac{W_{\text{HNO}_3}}{M_{\text{HNO}_3}} + \frac{W_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \right\}_{i-1} - L_i \left\{ 2 \frac{W_{\text{HNO}_2}}{M_{\text{HNO}_2}} + 3 \frac{W_{\text{HNO}_3}}{M_{\text{HNO}_3}} + \frac{W_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \right\}_i = 0
 \end{aligned} \tag{12}$$

$$G_{i+1}(Y_i)_{i+1} = G_i(Y_i)_i \tag{13}$$

In these equations  $G$  and  $L$  are the gas molar flow rate and the liquid mass flow rate respectively. Subscript  $i$  refers to the plate number with the usual convention

that streams labeled  $i$  exit from the same equilibrium stage.  $Y_i$  represents the mole fraction of inert component, O<sub>2</sub> or N<sub>2</sub>.

The following equations relate the compositions of the phases at equilibrium

$$PK_b = \frac{Y_{N_2O_4}}{Y_{NO_2}^2} \quad (14)$$

$$PK_c = \frac{Y_{N_2O_3}}{Y_{NO}Y_{NO_2}} \quad (15)$$

$$PK_d = \frac{Y_{HNO_2}^2}{Y_{NO}Y_{NO_2}Y_{H_2O}} \quad (16)$$

$$PK_e = \frac{Y_{HNO_3}^2Y_{NO}}{Y_{NO_2}^3Y_{H_2O}} \quad (17)$$

$$P^2K_2 = \frac{W_{HNO_2}^2}{Y_{NO}Y_{NO_2}} \quad (18)$$

$$P^2K_3 = \frac{W_{HNO_3}^2Y_{NO}}{Y_{NO_2}^3} \quad (19)$$

$$Y_{H_2O} = \frac{P_{H_2O}}{P} \quad (20)$$

The vapor pressure of water,  $p_{H_2O}$ , is given by Eq. (9) at 25°C.

Equations (10) to (20) may be solved for an  $N$ -stage absorption column when the entering gas and liquid compositions are given. If gas and liquid flow rates may be assumed to be approximately constant, only two material balances are required in combination with the equilibrium relationships.

A Gauss–Siedel iterative procedure may be conveniently set up for the solution of Eqs. (10) and (11) in combination with the equilibrium relationships (14) to (20). The procedure is rapidly convergent when  $(W_{HNO_3})_i$  is calculated from Eq. (11) and  $(W_{HNO_2})_i$  from Eq. (10). In this case the initial guess of column concentration profiles is not critical and accurate solution may be found.

## RESULTS AND DISCUSSION

The equilibrium stage model developed in the previous section has been used for the analysis of a nitric acid scrubbing column. The model contains no adjustable parameter and the values of various physicochemical constants are derived from literature information. The effects of number of equilibrium stages, nitric acid strength, liquid-to-gas flow rate ratio, HNO<sub>2</sub> concentration in the scrubbing liquid and initial NO<sub>x</sub> concentration have been investigated numerically. All the simulations reported here refer to dilute nitrogen oxides mixtures which have been saturated with water vapor at 25°C. The column pressure and temperature are 1 atm and 25°C respectively. The ratio  $Y_{NO}/Y_{NO_2}$  is in all cases equal to 10.



Two parameters are used to measure the performance of the oxidation-absorption process: the  $\text{NO}_x$  removal and the degree of oxidation of the scrubbed gas. The latter is defined as

$$\alpha = \frac{Y_{\text{NO}_x} - Y_{\text{NO}}}{Y_{\text{NO}_x}}$$

where  $Y_{\text{NO}_x}$  represents the total mole fraction of nitrogen oxides in any oxidation state

$$Y_{\text{NO}_x} = Y_{\text{NO}} + Y_{\text{NO}_2} + 2Y_{\text{N}_2\text{O}_3} + 2Y_{\text{N}_2\text{O}_4} + Y_{\text{HNO}_2} + Y_{\text{HNO}_3}$$

The degree of oxidation of the entering gas is about 14% in all simulations.

Figure 2 shows the calculated effect of the number of stages and the  $L/G$  ratio on  $\text{NO}_x$  removal. For a low  $L/G$  value the column becomes pinched at the top and only a limited degree of removal is achievable. Almost complete removal is obtained, however, if the  $L/G$  ratio is increased to about 2000 g/mol. The composition of the gas exiting from a six-stage process with the conditions given in Figure 2 is given in Table II. The degree of oxidation of this gas is about 87.7%.

Figures 3 and 4 show the effects of nitric acid concentration and number of stages on the  $\text{NO}_x$  removal and the degree of oxidation for two values of  $L/G$ . It is seen that as the nitric acid concentration is increased from a low value of 10 wt% the  $\text{NO}_x$  removal increases to reach a maximum value at an intermediate

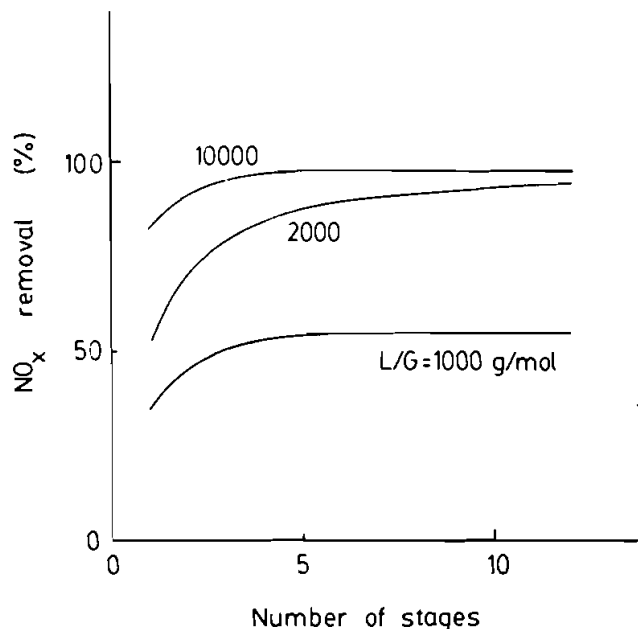


FIGURE 2 Effect of number of equilibrium stages at different  $L/G$  values.  $W_{\text{HNO}_3}^0 = 0.3$ ;  $W_{\text{HNO}_2}^0 = 1 \times 10^{-5}$ ;  $Y_{\text{NO}}^0 = 0.01$ ;  $Y_{\text{NO}_2}^0 = 0.001$ .

TABLE II

Exit gas composition.  $L/G = 2000$  g/mol;  $W_{\text{HNO}_3}^0 = 0.3$ ;  $W_{\text{HNO}_2}^0 = 1.0 \times 10^{-5}$ ;  $Y_{\text{NO}_x}^0 = 0.0116$ ;  $\alpha = 14\%$ ;  $P = 1.0$  atm;  $T = 25^\circ\text{C}$  and  $N = 6$

Component	Mole fraction
NO	$1.47 \times 10^{-4}$
$\text{NO}_2$	$9.38 \times 10^{-4}$
$\text{N}_2\text{O}_3$	$7.15 \times 10^{-8}$
$\text{N}_2\text{O}_4$	$5.71 \times 10^{-6}$
$\text{HNO}_2$	$6.74 \times 10^{-5}$
$\text{HNO}_3$	$3.66 \times 10^{-5}$
$\text{H}_2\text{O}$	$2.34 \times 10^{-2}$

acid strength. As the nitric acid strength is increased further  $\text{NO}_x$  removal drops and becomes negative when  $W_{\text{HNO}_3}$  becomes greater than about 0.4. In this case the  $\text{NO}_x$  concentration of the exit gas is higher than that of the entering gas.

The degree of oxidation (Figure 4) always increases, instead, as the nitric acid concentration is increased. Note that with a few equilibrium stages only and low acid strength, the degree of oxidation of the exiting gas is lower than the entering value. This occurs because the weak acid is in this case unable to oxidize NO to a great extent.  $\text{NO}_x$  absorption occurs then primarily via reaction (3). As the number of stages is increased the nitric acid scrubbing solution comes in contact

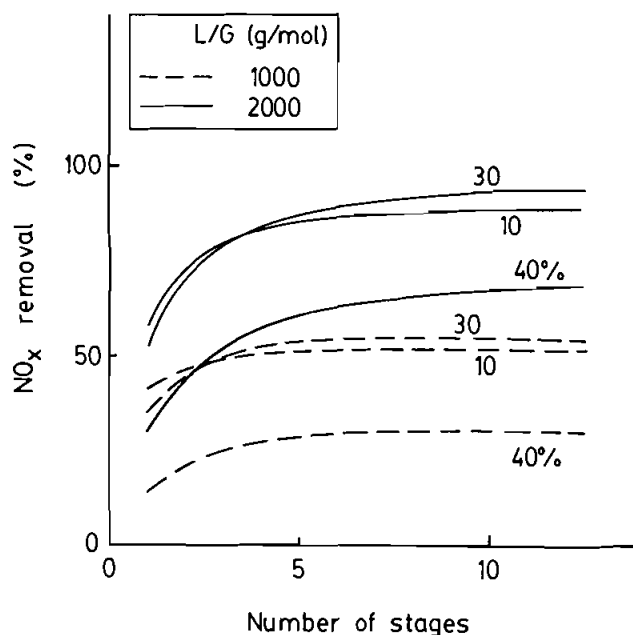


FIGURE 3 Effect of number of equilibrium stages at different nitric acid concentrations.  $W_{\text{HNO}_2}^0 = 1 \times 10^{-5}$ ;  $Y_{\text{NO}}^0 = 0.01$ ;  $Y_{\text{NO}_2}^0 = 0.001$

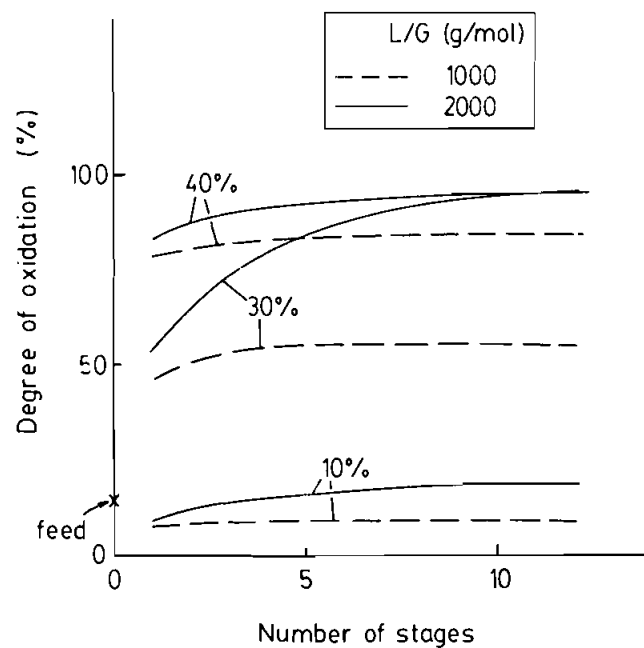


FIGURE 4 Effect of number of equilibrium stages at different nitric acid concentrations.  $W_{\text{HNO}_2}^0 = 1 \times 10^{-5}$ ;  $Y_{\text{NO}}^0 = 0.01$ ;  $Y_{\text{NO}_2}^0 = 0.001$ .

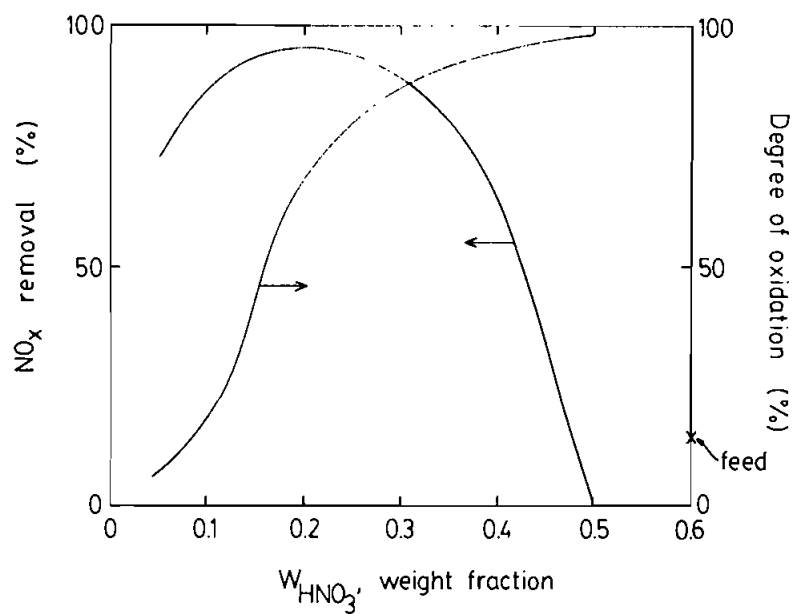


FIGURE 5 Effect of nitric concentration.  $W_{\text{HNO}_2}^0 = 1 \times 10^{-5}$ ;  $Y_{\text{NO}}^0 = 0.01$ ;  $Y_{\text{NO}_2}^0 = 0.001$ ;  $N = 6$ .

with nitrogen oxides having a lower degree of oxidation and is thus able to oxidize NO.

The results of these calculations are summarized in Figure 5 for  $N=6$ . A maximum NO<sub>x</sub> removal may be achieved with 15–25% nitric acid solutions. More concentrated solutions lead to lower NO<sub>x</sub> removal for the given inlet gas composition. The degree of oxidation of the exit gas increases as the nitric concentration is increased, but drops below the feed value if  $W_{\text{HNO}_3}$  is smaller than about 10%. This is the typical situation encountered in the manufacture of nitric acid. In this case NO<sub>x</sub> with the high degree of oxidation are contacted countercurrently with water or very dilute acid. Therefore the degree of oxidation tends to decrease toward the top of the column while nitric acid is formed. For pollution control the situation is reversed. NO<sub>x</sub> with low degree of oxidation are contacted with nitric acid. This oxidizes NO to HNO<sub>2</sub> while nitric acid is consumed.

It should be noted that from a practical point of view it may be advantageous to operate with a lower degree of NO<sub>x</sub> removal, say 80%, but with a high degree of oxidation. Complete NO<sub>x</sub> removal may then be accomplished with a final alkaline scrubbing operation.

Figure 6 shows the effect of nitrous acid concentration in the scrubbing liquid. Both NO<sub>x</sub> removal and degree of oxidation decrease as  $W_{\text{HNO}_2}$  is increased. Eventually, at high HNO<sub>2</sub> concentrations, nitrogen oxides are *stripped* from the liquid.

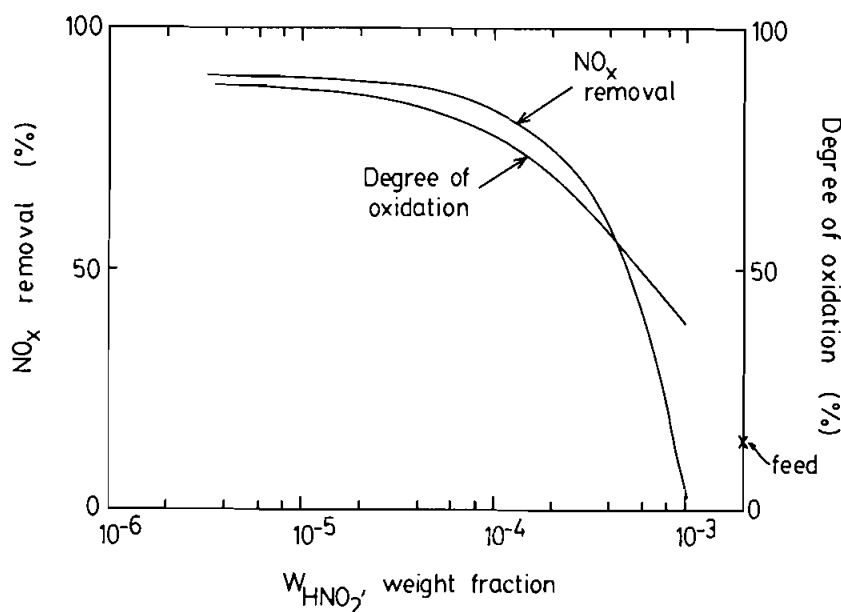


FIGURE 6 Effect of inlet HNO<sub>2</sub> concentration in scrubbing liquid.  $W_{\text{HNO}_3}^0 = 0.3$ ;  $Y_{\text{NO}}^0 = 0.01$ ;  $Y_{\text{NO}_2}^0 = 0.001$ ;  $N = 6$ .

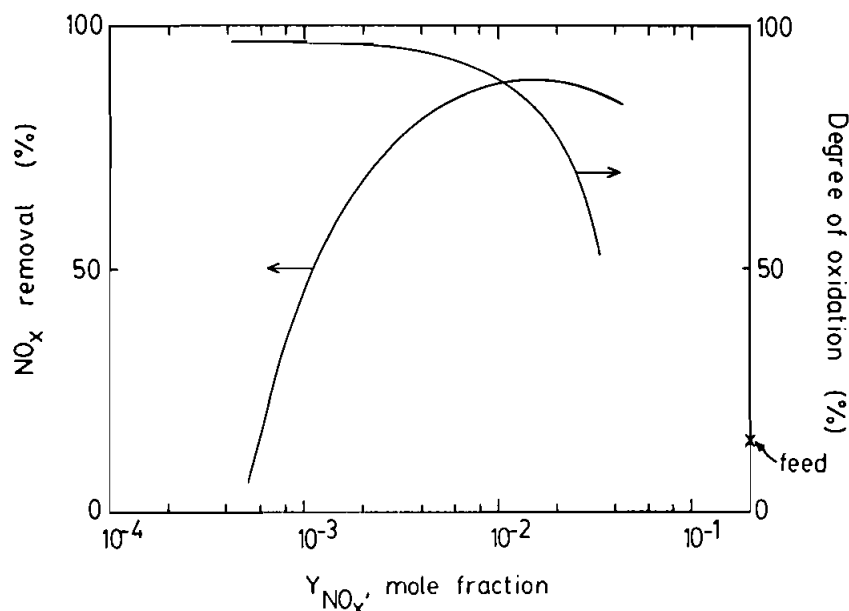


FIGURE 7 Effect of inlet NO<sub>x</sub> concentration.  $W_{\text{HNO}_3}^0 = 0.3$ ;  $W_{\text{HNO}_2}^0 = 1 \times 10^{-5}$ ;  $\alpha = 0.14$ ;  $N = 6$ .

Figure 7 shows the effects of the entering NO<sub>x</sub> concentration. The degree of oxidation of the entering gas is kept constant at about 14%. As seen from the graph, the oxidation-scrubbing efficiency decreases as the NO<sub>x</sub> concentration decreases. Figure 7 shows, however, that with 6 equilibrium stages 50% NO<sub>x</sub> removal and a very high degree of oxidation may be obtained in the 1000 ppm range of NO<sub>x</sub> concentrations.

Qualitatively similar results can be obtained at higher operating pressures, such as those encountered in the manufacture of nitric acid. Higher removal efficiencies may be achieved in this case with substantially lower liquid-to-gas flow rate ratios. For instance, for conditions analogous to those of Figure 7, 50% NO<sub>x</sub> removal may be obtained from a gas containing 1000 ppm of nitrogen oxides with an *L/G* ratio of only 140 g/mol at 7 atm total pressure.

## CONCLUSIONS

An equilibrium stage model has been developed for the analysis of an oxidation-absorption process for the removal of nitrogen oxides present in dilute gaseous streams. The model accounts explicitly for the complex nitrogen oxides chemistry using available literature information.

The results of numerical calculations show that nitric acid solutions of intermediate strength may be used as efficient scrubbing agents for gases with low degree of oxidation. An optimum nitric acid strength exists that permits oxidation

of NO in the liquid phase while still allowing simultaneous absorption and reaction of higher oxides of nitrogen. The optimum strength depends upon the composition of the feed gas. As shown by the equilibrium model, the oxidizer-scrubber works in reverse fashion to the process for the manufacture of nitric acid. For pollution control a nitric acid solution is fed at the top of a countercurrent column, while dilute NO<sub>x</sub> with low degree of oxidation are fed at the bottom. The scrubbed nitrogen oxides accumulate in the scrubbing liquid in the form of HNO<sub>2</sub>. This may be subsequently removed by stripping at higher temperature or by oxidation to HNO<sub>3</sub>.

Our equilibrium model may be effectively used in the analysis of the process and in the assessment of optimal operating conditions.

### NOMENCLATURE

$G$	gas molar flow rate, mol/s
$K$	equilibrium constant, atm <sup>-1</sup>
$K'$	equilibrium constant, atm <sup>-1/2</sup>
$K_x$	equilibrium constant for gas phase reaction $x$ , atm <sup>-1</sup>
$K_j$	equilibrium constant for heterogeneous reaction $j$ , atm <sup>-2</sup>
$L$	liquid mass flow rate, g/s
$M_x$	molecular weight of component $x$ , g/mol
$N$	number of theoretical stages
$p_x$	partial pressure of component $x$ , atm
$P$	total system pressure, atm.
$Y_x$	mole fraction of component $x$
$W_x$	weight fraction of component $x$

### Greek letters

$\alpha$	degree of $N$ -oxidation in gas phase
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### Subscripts

$i$	stage number
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### Superscripts

0	entrance conditions
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