

An Investigation of Nitrogen Oxide Absorption in Packed Columns

by

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Abstract

Experiments have been conducted to evaluate the performance of a packed column and its suitability in the study of the factors that influence the absorption mechanism of the nitrogen oxides (NO_x). These experiments were conducted in two packed columns, one fitted with wall wiper rings (to reduce the wall effects) and the other without. Both columns were packed with stainless steel lessing rings and operated at fixed gas and liquid flow rates (40 & 0.8 l/min, respectively), pressure (atmospheric), temperature (25 °C) and sodium hydroxide concentration (8% w/w). The NO_2^* ($\text{NO}_2^* = \text{equilibrium concentration of NO}_2 \text{ and N}_2\text{O}_4$) feed concentrations of up to 7000 ppm were used.

There was an improved performance in the packed column with wall wiper rings, suggesting that they reduce the wall effects. A mathematical model based on the interphase mass transfer conditions, reaction kinetics and equilibrium data present was used to interpret the absorption mechanism. Calculated column absorption efficiencies were found to agree with the experimental results for the column with wall wiper rings.

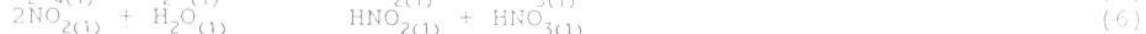
Introduction

Absorption of NO_x in packed columns is of special interest to the fertilizer, nuclear power industries and for control of static industry generated NO_x . It is important, therefore, to know whether the current theories of absorption with chemical reaction together with the published mass transfer and chemical kinetic absorption characteristics of the species involved are capable of describing and predicting the performance of the packed column.

The extensive published literature^[1-4] on experimental and theoretical studies of nitrogen dioxide absorption was consulted for parameter values to be used in the model predictions, and those well established parameters giving the best fit were adopted in the predictive model.

Theory

The following equilibria and reactions are believed to take place during NO_2^* absorption into aqueous solutions.



In the presence of the OH^- ions the hydrolysis products of reactions

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5 and 6 are rapidly neutralised as follows.



Among several publications regarding the absorption of nitrogen dioxide into sodium hydroxide solutions,⁽⁵⁻⁹⁾ the model proposed by Karlsson (1984) has been adopted following a thorough investigation of other models. This model assumes that both species of the equilibrium gas mixture (ie NO_2 and N_2O_4) diffuse to the gas liquid interface where they physically dissolve and diffuse, also at equilibrium, into the liquid. The N_2O_4 reacts continuously with the water solvent to form equimolar concentrations of HNO_2 and HNO_3 within the liquid phase. This hydrolysis reaction is assumed to be irreversible in alkaline solution since the hydrolysis products are rapidly neutralised.

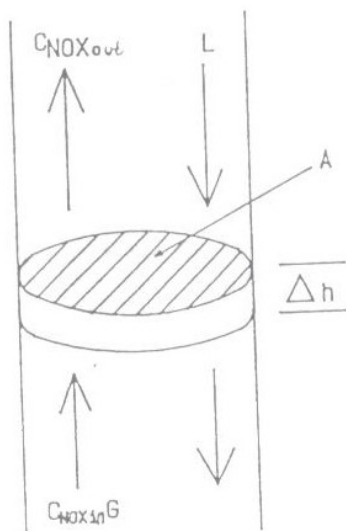


FIGURE 1 INCREMENTAL VOLUME OF THE ABSORPTION COLUMN

Consider the incremental volume of the absorption column shown in Figure 1. The Mass balance across the differential volume of the column yields;

$$G \frac{(\text{NO}_2^*)|_h - (\text{NO}_2^*)|_{h+\Delta h}}{\Delta h} = a A R_3 \quad (9)$$

$$\lim_{\Delta h \rightarrow 0} \frac{(\text{NO}_2^*)|_h - (\text{NO}_2^*)|_{h+\Delta h}}{\Delta h} = \frac{d(\text{NO}_2^*)}{dh} = \frac{a A R_3}{G} \quad (10)$$

$$\int_{(\text{NO}_2^*)_{in}}^{(\text{NO}_2^*)_{out}} \frac{d(\text{NO}_2^*)}{R_3} = \frac{a A}{G} \int_{h=0}^{h=H} dh \quad (11)$$

Where R_3 is given by the Karlsson rate expression.^[9]

$$R_3 = 2 \sqrt{kD_2 \left(\frac{2\xi}{3} + 1 \right) K_L C_1^2} \quad (12)$$

$$\text{where } \xi = \frac{C_1 D_1}{2 C_2 D_2}$$

Equation 12, on transformation gives the following equation.

$$R_3 = 2 \sqrt{k D_2 \bar{H}_2^2 (N_2O_4)_i^2 + \frac{k D_1 \bar{H}_2^{1.5} (N_2O_4)_i^{1.5}}{3\sqrt{K_L}}} \quad (13)$$

Substituting for R_3 in equation 10;

$$\frac{-d(NO_2)_b}{2 \sqrt{k D_2 \bar{H}_2^2 (N_2O_4)_i^2 + \frac{k D_1 \bar{H}_2^{1.5} (N_2O_4)_i^{1.5}}{3\sqrt{K_L}}}} = \frac{a A d h}{G} \quad (14)$$

or

$$\frac{-d(NO_2)_b}{\sqrt{D_2 \bar{H}_2^2 (N_2O_4)_i^2 + \frac{D_1 \bar{H}_2^{1.5} (N_2O_4)_i^{1.5}}{3\sqrt{K_L}}}} = \frac{2 a A \sqrt{k} d h}{G} \quad (15)$$

$$\frac{-d(NO_2)_b}{\sqrt{D_2 \bar{H}_2^2 (N_2O_4)_i^2 + \frac{D_1 \bar{H}_2^{1.5} (N_2O_4)_i^{1.5}}{3\sqrt{K_L}}}} = \lambda d h \quad (16)$$

$$\text{where } \lambda = \frac{2 a A \sqrt{k}}{G}$$

See Table i for model parameter values employed.

Table i : Model Parameters

Parameter	Units	Value	Reference
$\bar{H}(\text{kD})^{1/2}$	kmol/m ² atm.s	0.0047	4
K_L	m ³ /kmol	7.62E4	11
k	S ⁻¹	3460	calculated
\bar{H}_2	kmol/m ³ atm.s	2.04	11
D_2	m ² /s	1.40E-9	11
k_g	m/s	4.37E-2	4
k_1	m/s	3.75E-5	4
A	m ²	4.71E-3	
a	m ² /m ³	157	4
G	m ³ /s	6.67E-4	

Ali (1988) incorporated the gas phase mass transfer coefficient in the computation of the interfacial gas concentration of N_2O_4 , as follows.

$$(N_2O_4)_1 = \left(\frac{-g \pm \sqrt{g^2 + 4\alpha x}}{2\alpha} \right)^2 \quad (17)$$

where

$$g = \frac{k_g}{\sqrt{K_G}}$$

$$\alpha = (2k_2 + \mu)$$

$$\mu = 2\bar{H}_2 \sqrt{k_2 D_2}$$

$$x = g \sqrt{(N_2O_4)_b + 2k_g(N_2O_4)_b}$$

Substituting for $(N_2O_4)_i$ equation 16 gives;

$$\frac{-d(NO_2^*)_b}{\sqrt{D_2 \bar{H}_2^2 \left[\frac{-g \pm \sqrt{g^2 + 4\alpha x}}{2\alpha} \right]^2 + \frac{D_1 \bar{H}_2^{-1.5} \left[\frac{-g \pm \sqrt{g^2 + 4\alpha x}}{2\alpha} \right]^2}{3\sqrt{K_L}}} = \lambda dh \quad (18)$$

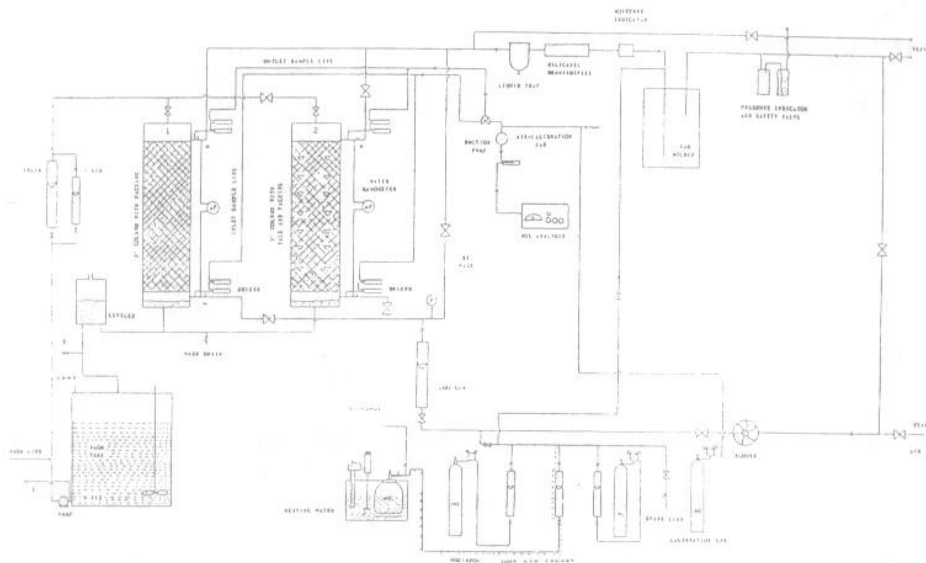
Calculations for the above equation proceed stepwise from the inlet gas condition at the bottom of the column to the outlet condition at the bed height of the column. The liquid phase mass transfer coefficient (k_1) does not enter into the model equation because the hydrolysis of N_2O_4 is a pseudofirst order reaction.⁽²⁾

Experimental Apparatus and Procedure

A schematic diagram of the experimental rig is shown in Figure 2. It consisted of two glass columns of 7.75 cm internal diameter, packed with 1.27 x 1.27 cm (diameter x length) stainless steel lessing rings to a height of about 87.7 cm. One column was fitted with wall wiper rings having triangular tags to reduce the wall effects so that the plug flow pattern could be approached more closely in both phases. Sodium hydroxide solution and dry process air were separately manually controlled by floatmeters to the top and bottom of the column, (in one column at a time), respectively. The absorption was performed under steady state conditions at atmospheric pressure, 298 K, constant liquid and gas flow rates (0.8 and 40 l/min, respectively) and constant NaOH concentration (8% w/w).

The feed and effluent gaseous NO_2^* concentrations were measured by a chemilumnescent gas NO_x/NO analyser (Grubb Parson Chemitox). The gas and liquid mass transfer coefficients, and the interfacial area under the same flow conditions were previously determined by absorbing carbon dioxide into a buffer solution of sodium carbonate and sodium bicarbonate, and by absorbing sulphur dioxide into sodium hydroxide solution.⁽¹⁰⁾

Figure 2: General Purpose Absorption Rig



Results and Discussion

Figure 3 shows the calculated and observed variation in absorption efficiency with NO_2^* feed concentration, for both columns. There is about 10% increase in the column absorption efficiency in favour of the tagged column. This suggests that the wall wiper rings enhances the column performance by reducing the wall effects, due to the channeling and bypassing. The model predictions employing the parameters specified later are in good agreement with the performance data from the tagged column over the whole range of NO_2^* concentrations used in the present study.

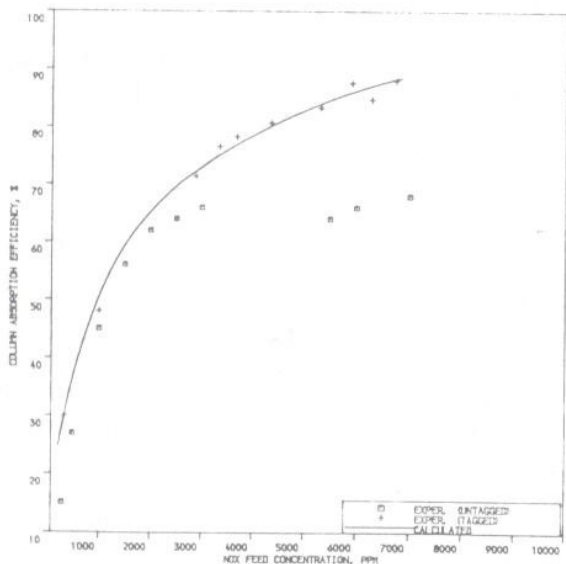


FIGURE 3. RELATIVE COLUMN ABSORPTION EFFICIENCY OF NO_2^* IN TAGGED AND UNTAGGED COLUMN

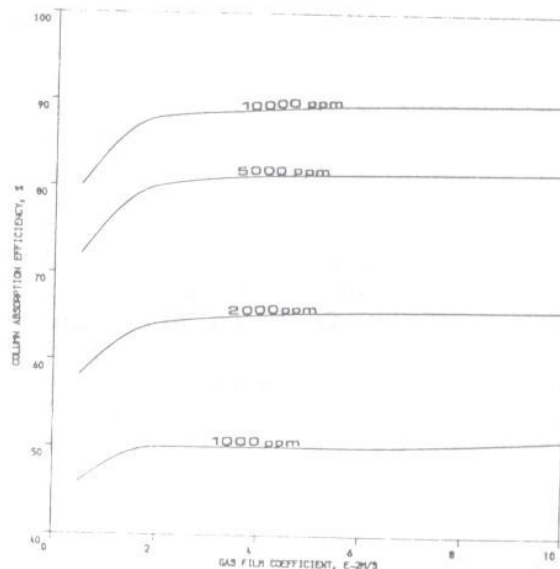


FIGURE 4. EFFECT OF GAS PHASE MASS TRANSFER COEFFICIENT ON ABSORPTION EFFICIENCY OF THE TAGGED COLUMN (AT SPECIFIC CONCENTRATIONS)

As for the untagged column the observed column efficiency levels off for NO_2^* concentrations above 3000 ppm. This can be explained on the basis of the flow patterns present in the column. In model derivation it is assumed that the gas and liquid flow in the piston or plug flow pattern with flat mean velocity profiles across the column, however, axial dispersion may be present. For columns with small diameters, liquid maldistribution may lead to channelling or local regions where the liquid flow is abnormally great, also the liquid in the static holdup moves forward much more slowly than in the dynamic holdup, and small liquid droplets falling from a packing piece may be blown upward by the local gas flow. Similarly resistance to gas flow at the column walls and in the relatively dry regions of the packing is different from that present elsewhere. Downwards movement of the gas may even induce local downward movement of the gas. All these phenomena result in axial dispersion and this effect is more pronounced at high gas concentrations due to the higher absorption rates present. The wall wiper rings partially reduce this effect by redirecting the liquid and gas away from the wall of the column towards the main streams of the column.

The experimentally determined values of interfacial area, gas and liquid mass transfer coefficients were $130 \text{ m}^2/\text{m}^3$, $3.95\text{E-}2 \text{ m/s}$ and $3.92\text{E-}5 \text{ m/s}$ (for untagged column), and $157 \text{ m}^2/\text{m}^3$, $4.37\text{E-}2 \text{ m/s}$ and $3.75\text{E-}5 \text{ m/s}$ (for tagged column), respectively.⁽⁴⁾

Model parametric analysis shows that the gas phase mass transfer coefficient (k_g) only slightly affects the column performance when the k_g is greater than $3.0\text{E-}2 \text{ m/s}$, see Figure 4. Below this value the column absorption efficiency is highly influenced by the gas film resistance. It may be concluded, therefore, that with the k_g value found in the present system, the gas film resistance may be neglected without causing significant error in the model predictions.

Figure 5 shows the calculated absorption efficiencies obtained by employing the values of absorption coefficients $(\bar{H}/kD)_{\text{N}_2\text{O}_4}$ as reported by other research workers. It can be seen that the value of $0.0047 \text{ kmol/m}^2 \text{ atm.s}$ gives predictions which are in relatively good agreement with the experimental observation. Taking the literature recommended values of D and \bar{H} as being equal to $1.40\text{E-}9 \text{ m}^2/\text{s}$ ⁽¹¹⁾ and $2.04 \text{ kmol/m}^3 \text{ atm}$ ⁽²⁾ the pseudo-first order hydrolysis constant for N_2O_4 computes to 3460 s^{-1} .

Figure 6 shows the calculated variation of NO_2^* concentration with the column height. It can be seen that at high NO_2^* concentrations there is a sharp fall in NO_2^* concentration in the first quarter of the column and a more gradual fall in the last quarter of the column. At lower NO_2^* concentrations (ie $< 500 \text{ ppm}$) there is an insignificant drop in the concentration. As should be expected at high NO_2^* concentrations the absorption rate is high due to high driving force, with consequently a sharp drop in the NO_2^* concentration, whereas at lower concentrations the slow physical absorption of NO_2 is more predominant. It may be concluded that when low concentrations of NO_2^* are to be absorbed the conventional packed column is not very suitable for gas cleaning by alkaline absorption.

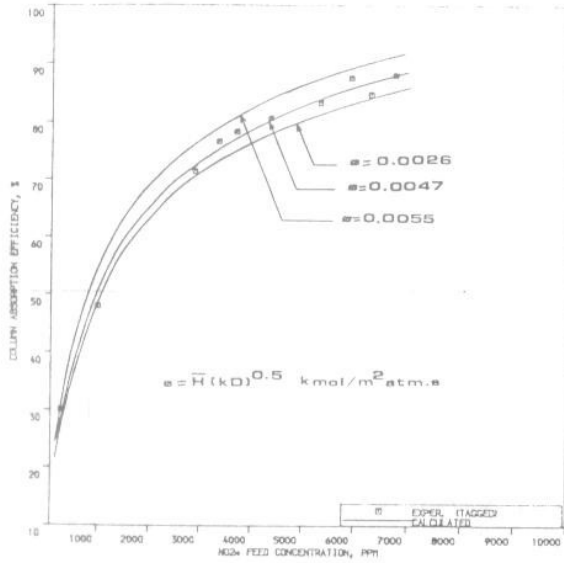


FIGURE 5. SELECTION OF A SUITABLE ABSORPTION COEFFICIENT TO BE USED IN THE MODEL

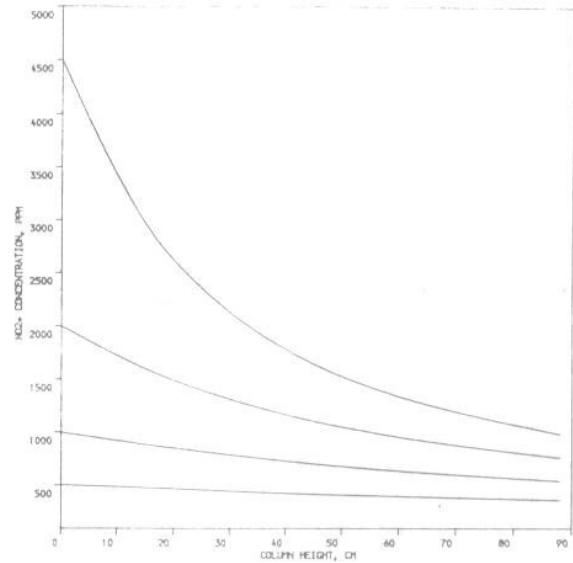


FIGURE 6. CALCULATED VARIATION OF NO₂* CONCENTRATION WITH COLUMN HEIGHT

Conclusion

The agreement between the model predictions and the experimental observation justifies the assumption that, for the concentrations covered in the present study, the simultaneous diffusion, dimerization and hydrolysis of NO₂ and N₂O₄ control the overall rate of NO₂* absorption. The improved performance of the tagged column implies that the wall wiper rings do enhance countercurrent plug flow pattern. Therefore, under suitable controlled operating conditions, the tagged column may be used to study in more details the different factors influencing the continuous steady state countercurrent absorption of NO_x, as reported in other publications.⁽¹²⁻¹⁴⁾

Nomenclature

- A = cross-section area of bed, m²
 a = interfacial area, m⁻¹
 C = liquid phase molar concentration, kmol/m³
 D = diffusivity, m²/s
 G = gas flow rate, m³/s
 \bar{H} = Henry's solubility constant, kmol/m³.atm
 k = pseudo-first order hydrolysis rate constant, s⁻¹
 k_g = gas phase mass transfer coefficient, m/s
 k_l = liquid phase mass transfer coefficient, m/s
 K_G = gas phase equilibrium constant, atm⁻¹
 K_L = liquid phase equilibrium constant, m₃/kmol
 R = absorption rate, kmol/m²s

Others

- () = gas phase species concentrations, kmol/m³
 (NO₂*) = (NO₂ + 2(N₂O₄)) at equilibrium

Subscripts

1	=	NO_2
2	=	N_2O_4
3	=	NO_2^*
b	=	bulk
g	=	gas
l	=	liquid
i	=	gas-liquid interface

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