

# Absorption of Nitrogen Oxides into Sodium Hydroxide Solution in a Packed Column: Effect of Gas Flowrate and Temperature.

by

J.H.Y Katima\*      A. Azapagic\*\* and D. Handley\*\*\*

## Abstract

The effect of gas flow rate and temperature on the absorption rate of nitrogen oxides ( $\text{NO}_x$ ) and column absorption efficiency has been studied using a 2M sodium hydroxide (NaOH) solution in a packed column. The absorption process was carried out at atmospheric pressure, with  $\text{NO}_x$  concentration ranging between 150 and 10000 ppm,  $\text{NO}/\text{NO}_2$  ratio of 0.5 and liquid flow rate of 0.8 l/min. The gas flow rate was varied from 20 to 60 l/min and the temperature from 25 to 45 C.

It was found that the column absorption efficiency increases with decreasing gas flow rate, however, the varying gas flow rate has no significant influence on the mean absorption rate.

The column absorption efficiency also increases with a decreasing temperature down to 25 C. A further decrease in temperature (below 20 C) causes a decrease in the column performance. The varying temperature appear to have no influence on the mean absorption rate.

## Introduction

Absorption of nitrogen oxides  $\text{NO}_x$  into alkaline solutions is an important operation in several industrial processes as well as in  $\text{NO}_x$  emission control. It has been studied extensively, but because of its complexity, there remains a scope for research to enhance overall understanding of this process and the factors affecting it.

The effect of gas flow rate has been studied by several investigators.<sup>(1-6)</sup> Chambers and Sherwood<sup>(1)</sup> conducted their study in a wetted column and found that the  $\text{NO}_x$  absorption rate was proportional to approximately the 0.8 power of gas velocity. They concluded that  $\text{NO}_x$  diffusional resistance was the controlling step. Joshi et al,<sup>(2)</sup> using a packed column, also reported that the  $k_g a$  increases and thus the absorption rate increased with the gas flow rate. Gray and Yoffe<sup>(3)</sup> observed a 20% increase by changing the gas flow from Reynolds number 4450 to 11100. On the contrary, Caudle and Denbigh<sup>(4)</sup> found that in cases of low  $\text{NO}_x$  concentrations (< 10000 ppm) the absorption rate appears to be less dependent on the gas flow rate.

On the other hand, Counce and Perona<sup>(5)</sup> and Selby and Counce<sup>(6)</sup> observed a falling column absorption efficiency with increasing gas flow rate. This was attributed to the reduced gas residence time in the column.

It is logical to expect that, despite the increase in  $k_g a$ , the increase in gas flow rate may affect other hydrodynamic parameters of the column and the equilibrium behaviour of the entire system. These may increase or decrease the absorption rate and/or column performance. For example, short residence times may mean that the

\* University of Dar es Salaam, Tanzania

\*\* University of Tuzla, Yugoslavia

\*\*\* University of Leeds, UK

gas phase equilibrium, especially that of  $\text{HNO}_2$ , is not fully attained in most parts of the column, so that most parts of the column will be exposed to less soluble and less reactive  $\text{NO}$  and  $\text{NO}_2$ . The liquid holdup and effective interfacial area are also reported to be affected by the gas flow rate.<sup>[7]</sup>

The effect of temperature was studied by Counce and Perona,<sup>[8]</sup> Aoki et al<sup>[9]</sup> and Joshi et al. Counce and Perona and Aoki et al reported a decrease in  $\text{NO}_2$  absorption rate and column absorption efficiency with increasing temperature. They attributed this to the decrease in concentration of the more reactive  $\text{N}_2\text{O}_4$  with increasing temperature. Joshi et al however reported that between 10 and 45 C the temperature has a nominal influence on absorption rate, since solubility and  $\text{NO}$  oxidation rate decrease, whilst diffusion rate and reaction rate increase with increasing temperature. It may be assumed, therefore, that the opposing influence of these factors on absorption rate cancel each other. Below 10 C Joshi et al reported a fall in absorption rate down to 5 C.

This study was intended to explore more deeply the influence of temperature and gas flow rate, with the intention of advising on best operating conditions for the packed columns used in the control of emissions.

### Theory

A mechanism of  $\text{NO}_x$  absorption into alkaline solutions has been described in a paper by Katima and Handley.<sup>[10]</sup>

It is agreed that simultaneous absorption of high concentrations of  $\text{NO}$  and  $\text{NO}_2$  is predominantly controlled by dissolution with the fast pseudo-first order hydrolysis of  $\text{N}_2\text{O}_4$ ,<sup>[9-11]</sup> and at low  $\text{NO}_x$  concentrations by the gas phase formation and physical absorption of  $\text{HNO}_2$  as the major transport mechanism.<sup>[10,12,13,14]</sup>

### Experimental Apparatus and Procedure

A schematic diagram of the experimental equipment is shown in Figure 1. The absorption was carried out in a 7.75 cm i.d. glass column, packed with 1.27 cm stainless steel lessing rings to a height of 87.75 cm. The column was fitted with wall wiper rings to reduce wall effects so that a plug flow was approached closely.<sup>[15]</sup> The absorption of  $\text{NO}_x$  gas ( $\text{NO}/\text{NO}_2 = 0.5$ ) was carried out into a 2M  $\text{NaOH}$  solution at atmospheric pressure with a constant liquid flow rate of 0.8 l/min. The gas flow rate ranged from 20 to 60 l/min at constant temperature of 25 C. The liquid and gas streams were manually controlled with the aid of floatmeters to the top and bottom of the column, respectively. The influence of temperature on the absorption of  $\text{NO}_x$  was studied in the range of 15 to 45 C at a constant gas flow rate of 40 l/min. In all experiments  $\text{NO}_x$  feed concentrations were varied between 150 and 10000 ppm.

The feed and effluent gaseous  $\text{NO}_x$  concentrations were measured by a chemiluminescent gas  $\text{NO}_{x/\text{NO}}$  analyzer (Grubb Parson Chemitox). The starting and final  $\text{NaOH}$  concentrations were determined by a standard titrimetric method.

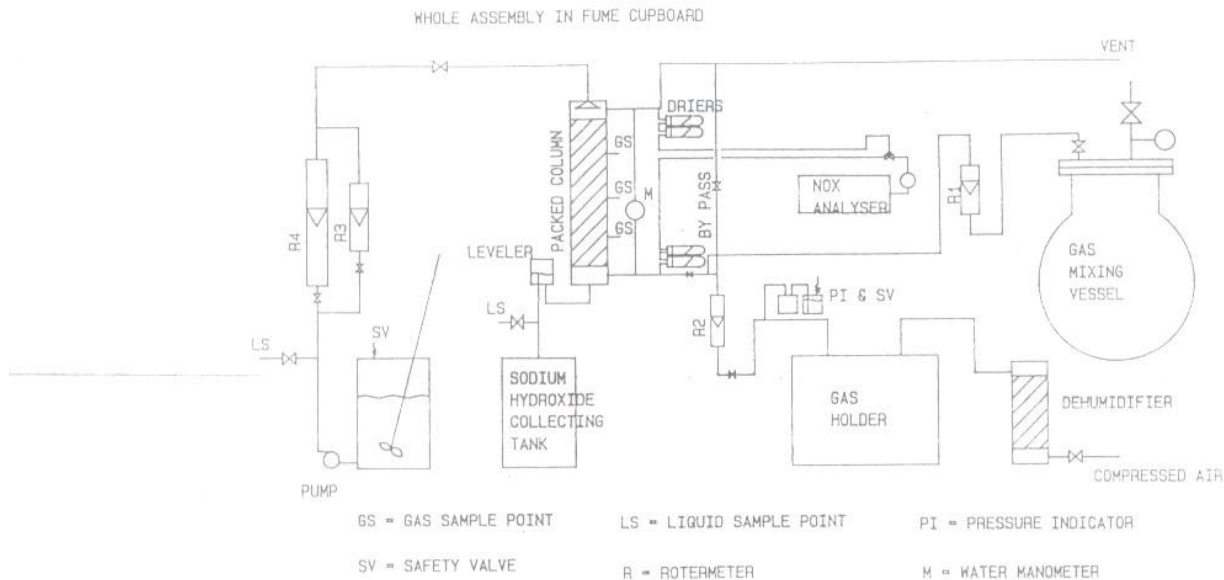


FIGURE 1 GENERAL PURPOSE ABSORPTION RIG

## Results and Discussion

### 1) Effect of Gas Flow Rate

In the following discussion, the calculated results refer to application of the model presented in a previous paper by Katima and Handley<sup>[10]</sup>

The experimental and predicted variation of absorption efficiency with  $\text{NO}_x$  feed concentration for different gas flow rates is shown in Figure 2. It is worth mentioning that the model assumes that the gas flow rate has no influence on the column hydrodynamic behaviour (ie on  $k_a$ , liquid holdup and axial dispersion) and gas phase equilibrium (ie it assumes gas phase equilibrium exists along the entire column height). It can be seen that at 50 and 60 l/min gas rates the predictions are not in good agreement with the experimental data, which may mean that the above assumptions do not hold at high gas rates, however, it can be seen that the column absorption efficiency decreases with the increasing gas flow rate. On increasing the gas flow rate from 20 to 60 l/min the column absorption efficiency decreased by about 20% at low  $\text{NO}_x$  concentrations (< 1000 ppm) and by about 8% at high  $\text{NO}_x$  concentrations (> 7000 ppm). This may be attributed to an increase in the gas loading of the column for the reasons given below.

A short residence time in the column could mean that the equilibrium formation of  $\text{HNO}_2$  is not being completely attained in most parts of the column, leading to higher  $\text{NO}_x$  concentrations at the outlet as is evident in Figure 3. The disagreement between experimental and calculated concentrations towards the top part of the column, supports the suspicion that the gas flow rate does significantly influence the equilibrium behaviour of the system. For example, as the concentration changes along the column, the model predicts that the contribution of  $\text{HNO}_2$  to the absorption process should begin to dominate.<sup>[10]</sup> Since the equilibrium between  $\text{HNO}_2$ ,  $\text{NO}$ - $\text{NO}_2$  and  $\text{H}_2\text{O}$  may not be fully established, the downstream parts of the column would experience higher concentrations of the less reactive  $\text{NO}$  and  $\text{NO}_2$ , so that the predicted concentration gradient is 'greater than' the observed one.

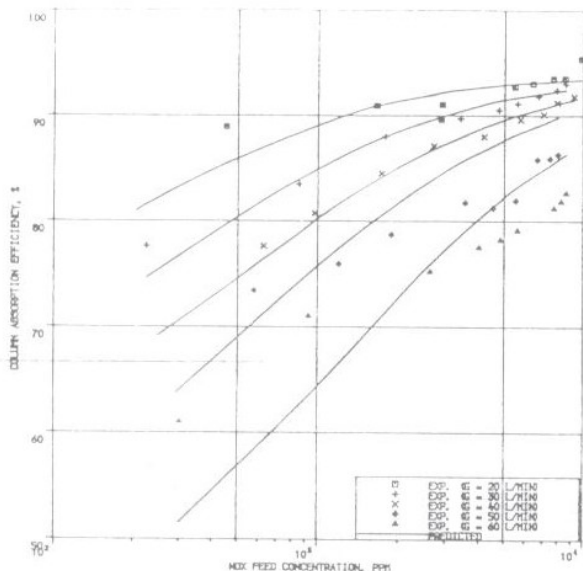


FIGURE 2 . EFFECT OF GAS FLOW RATE ON COLUMN ABSORPTION EFFICIENCY (NO/NO2 = 0.5)

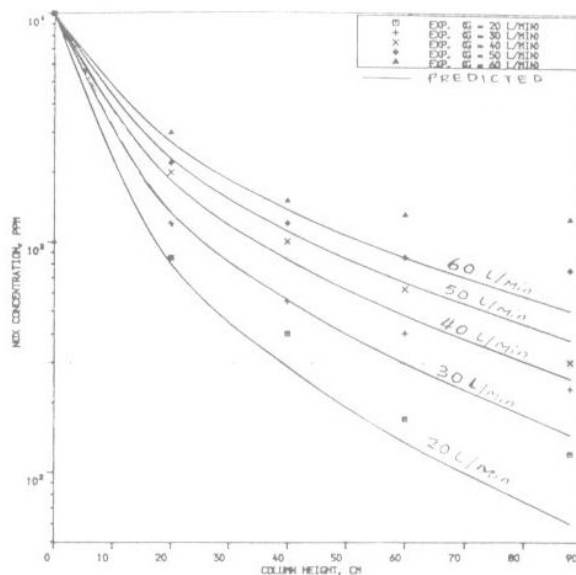


FIGURE 3 . EFFECT OF GAS FLOW RATE ON NOx CONCENTRATION GRADIENT (NO/NO2 = 0.5 AND NOx CONC. = 10000 PPM)

The reduction in NO<sub>x</sub> concentration gradient means that all points in the column experience relatively higher NO<sub>x</sub> concentrations. This behaviour, coupled with the possibility of an increase in gas phase mass transfer coefficient ( $k_g$ ) will lead to an increase in the mean absorption rate. In contrast to the above behaviour, the experimental data in Figures 4 and 5 show that the gas flow rate does not have a significant influence on the mean NO<sub>x</sub> absorption rate, which is in agreement with the findings of Caudle and Denbigh.<sup>[4]</sup> This suggests that there are a number of factors which are oppositely influenced by the gas flow rate, so that they cancel each other. For example, Shuman et al,<sup>[7]</sup> reported that at low liquid flow rates (the liquid rates they used ranged between 0.68 and 13.58 kg/m<sup>2</sup>s whereas in the present study 2.83 kg/m<sup>2</sup>s was used) an increase in the gas flow rate increases the operating holdup which in turn decreases the effective interfacial area. The decrease in effective interfacial area directly reduces the absorption rate, whereas the increase in operating liquid holdup means an appreciable portion of the void space in the packing is occupied by liquid leaving much less free space for the gas to flow. The latter effect will result in local gas jetting, reduced gas residence time and lower HNO<sub>2</sub> concentrations thus reducing the column absorption rate.

The following correlations may be used to demonstrate the expected behaviour of different factors as a result of varying gas flow rate. It should be borne in mind, that these correlations give an expected trend rather than an actual change.

Shulman et al proposed that;

$$j_D = \left[ \frac{k'_g M'_m P_{Bm}}{G'} \right] \left[ \frac{\mu'_G}{P'_g D'_v} \right]^{\frac{2}{3}} = 1.195 \left[ \frac{d'_p G'}{\mu'_G (1-e')} \right]^{-0.36} \quad (1)$$

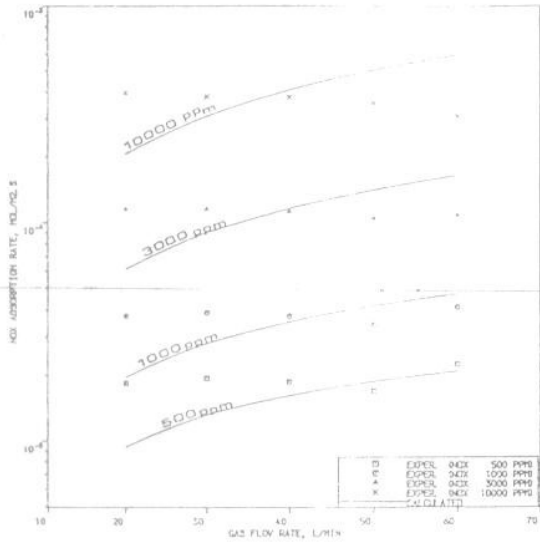


FIGURE 4 EXPERIMENTAL AND CALCULATED EFFECT OF GAS FLOW RATE ON NOX ABSORPTION RATE (NO/NO2 = 0.5)

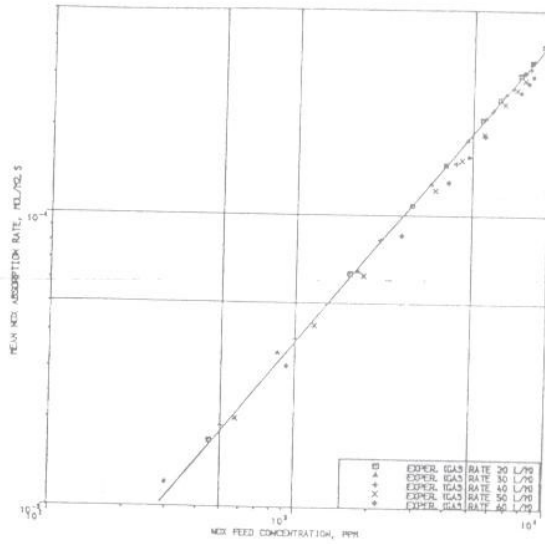


FIGURE 5 EFFECT OF GAS FLOW RATE ON MEAN NOX ABSORPTION RATE (NO/NO2 = 0.5)

$$k_g = \frac{1.195 \left[ \frac{d_p' G'}{\mu_g' (1 - e')} \right]^{-0.36} \frac{G'}{M_{im} \rho_{Bm}}}{\left[ \frac{\mu_g'}{\rho_g' D_v'} \right]^{\frac{2}{3}}} \quad (2)$$

Where

$$e' = e - h_t \quad (3)$$

$$h_t = h_s + h_o \quad (4)$$

Shulman et al reported that  $h_s$  is independent of varying gas rate and proposed that;

$$h_s = 2.75 \frac{\mu_L^{0.02} \sigma^{0.99}}{\rho_L^{0.37}} \quad (5)$$

Von Stoker and Cevey<sup>[16]</sup> found that the operating holdup was influenced by varying gas flow rate, and proposed the following correlation.

$$h_o = 2.562 Re_L^{0.7} \times 10^{9.4E-5 Re_v Ga}^{-0.41} \quad (6)$$

Where

$$Re_L = \frac{L d_p}{\mu_L} \quad (7)$$

$$Ga_L = \frac{\rho_L^2 d_p^3 g}{\mu_L^2} \quad (8)$$

$$Re_G = \frac{u_g \rho_g d_p}{\mu_g} \quad (9)$$

Von Stoker and Cevey also observed that the gas flow rate has an influence on the liquid axial dispersion, and they proposed the following correlation for axial dispersion coefficient.

$$Pe = 2.593 Fr_L^{0.17} \times 10^{2.95 E-5 Re_g} \quad (10)$$

Where

$$Fr_L = \frac{L^2}{\zeta^2 d_p g} \quad (11)$$

$$Pe = \frac{U_L d_p}{D} \quad (12)$$

Shulman et al reported that at low liquid rate the effective interfacial area decrease with gas rate and that its behaviour, under varying gas rate, is similar to that of the wetted area.

$$\frac{a_w}{a_t} = \frac{a_e}{a_t} = 0.24 \left[ \frac{L'}{G'} \right]^{0.25} \quad (13)$$

Table 1 shows the predicted behaviour of various factors with varying gas flow rate according to the above correlations.

Table 1: Influence of Gas Flow Rate on Various Factors

	V , 1/min	20	30	40	50	60
ho,	m <sup>3</sup> /m <sup>3</sup>	0.0323	0.0326	0.0328	0.0331	0.0333
hs,	m <sup>3</sup> /m <sup>3</sup>			1.694 E-4		
e ,	m <sub>3</sub> /m <sub>3</sub>			0.825		
e' ,	m <sup>3</sup> /m <sup>3</sup>	0.7924	0.7922	0.7720	0.7917	0.7915
k ,	m/s	1.07E-2	1.39E-2	1.67E-2	1.92E-2	2.10E-2
Pe		0.5045	0.5057	0.5065	0.5077	0.5086
D,	m <sup>2</sup> /s	1.191E-3	1.188E-3	1.186E-3	1.183E-3	1.181E-3
a <sub>e</sub> /a <sub>t</sub>		0.577	0.5207	0.4846	0.4583	0.4878

Clearly it can be seen that the effects of  $k_g$  and effective interfacial area will tend to cancel each other. As shown on Figure 4 the predictions (assuming constant hydrodynamic parameters) are only in good agreement with the experimental data obtained at 40 l/min (at which flow rate the  $k_g$  and  $a_e$  were experimentally determined). This suggests that for the  $k_g$  and  $a_e$  should be determined at actual operating conditions.

It may concluded from experimental data that, under the experimental conditions used in this study, the gas rate has no significant influence on the column absorption rate. But it should be borne in mind that unnecessarily high gas rates will reduce the column efficiency.

The effect of temperature on column absorption efficiency is shown in Figures 6 and 7. It can be seen that the column efficiency decrease with the increasing temperature down to 25 C. The maximum observed decrease is about 5% and is more significant at lower NO<sub>x</sub> concentrations (< 1000 ppm), however at 15 C the absorption efficiency is lower than that at 45 C.

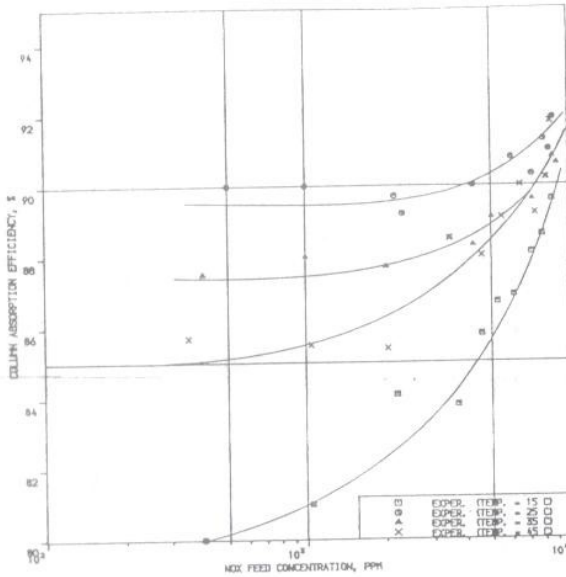


FIGURE 6 EFFECT OF TEMPERATURE ON COLUMN ABSORPTION EFFICIENCY (NO/NO<sub>2</sub> = 0.5)

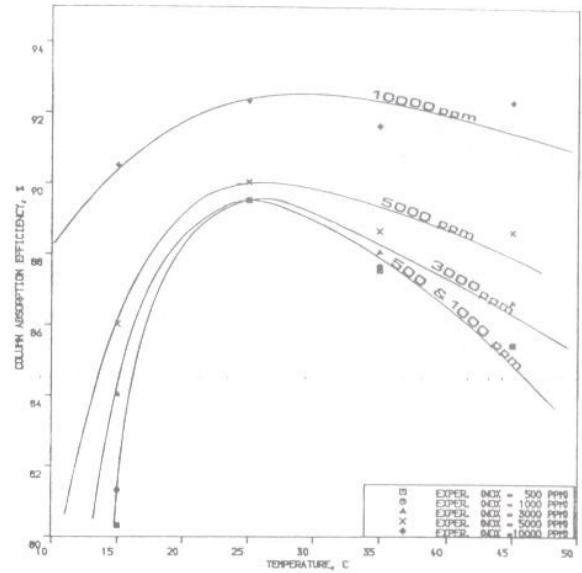


FIGURE 7 EFFECT OF TEMPERATURE ON COLUMN ABSORPTION EFFICIENCY (VARIOUS NO<sub>x</sub> CONCS., NO/NO<sub>2</sub> = 0.5)

The decrease in column absorption efficiency with increasing temperature may be attributed to the decrease in the higher molecular weight reactive species (ie N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>3</sub>) due to the nature of the gas phase equilibrium reactions, see following expressions.



Where

$$K_{N2O4} = \frac{P_{N2O4}}{P_{NO2}^2} \tag{16}$$

$$K_{N2O3} = \frac{P_{N2O3}}{P_{NO}P_{NO2}} \tag{17}$$

K<sub>N2O4</sub> and K<sub>N2O3</sub> may be computed by Bronsted<sup>[18]</sup> and Beatie and Bell<sup>[19]</sup> respectively.

$$ie : \log K_{N2O4} = \frac{2993}{T} - 9.226 \text{ atm}^{-1} \tag{18}$$

$$\log K_{N2O3} = \frac{2072}{T} - 7.234 \text{ atm}^{-1} \tag{19}$$

Increasing temperature also does not favour the equilibrium gas phase formation of NHO<sub>2</sub> which is an exothermic reaction so that more NO and NO<sub>2</sub> will pass through the column unaffected.

Decreasing temperature below 20 C causes a large decrease in the column performance. It can be seen from Figure 6 that column absorption efficiency at 15 C is much lower than at 45 C. It is well known that the reaction rate constant and diffusion rate decrease with decreasing temperature whereas the physical solubility of all the  $\text{NO}_x$  species as well as the equilibrium partial pressure of  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_3$  increase with the decreasing temperature. The overall effect of these opposing factors should result in the presence of a maxima in the column absorption efficiency as is evident in Figure 7. These opposing factors may cancel each other so that in practice, the temperature may appear to have no significant influence on the mean column absorption rate, see Figure 8. This is partly in agreement with the observation made by Joshi et al, who reported a fall in absorption rate below 10 C.

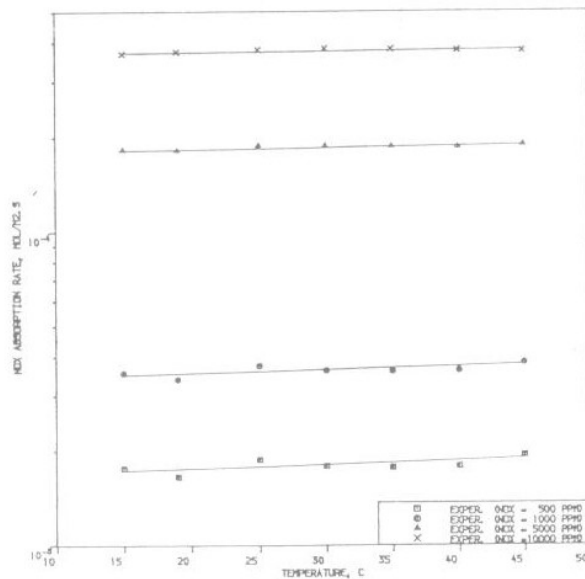


FIGURE 8 EFFECT OF TEMPERATURE ON NO<sub>x</sub> ABSORPTION RATE (VARIOUS NO<sub>x</sub> CONCENTRATIONS, NO/NO<sub>2</sub> = 0.5)

## Conclusion

The column absorption efficiency decreases with increasing gas flow rate as a result of reduced gas residence time and increased gas loading. The influence of gas flow rate on the mean absorption rate is insignificant, probably due to the opposing influence the gas flow rate has on different factors as explained previously. It may be concluded that for efficient removal of  $\text{NO}_x$  unnecessarily high gas rates should be avoided. If a large volume gas stream has to be treated a reasonably low gas superficial velocity should be ensured (eg less than  $0.2 \text{ kg/m}_2\text{s}$  when a liquid superficial velocity is about  $2.5 \text{ kg/m}_2\text{s}$ ) during a column design.

The column absorption efficiency appears to reach a maximum at 25 C, for the reasons discussed previously, however there is no indication of any significant influence of temperature on the mean absorption rate. It can be concluded, that for an efficient column performance, high liquid temperatures ( $>$  ambient) should be avoided. If large concentrations of  $\text{NO}_x$  have to be removed, the installation of a cooling heat exchanger to remove the exothermic heats of reaction and maintain a low exit gas stream humidity should be considered.



## Nomenclature

- $a_e$  = effective interfacial area,  $m^2/m^3$   
 $a_t$  = total interfacial area,  $m^2/m^3$   
 $a_w$  = wetted area,  $m^2/m^3$   
 $c_i$  = interfacial  $NO_x$  concentration,  $mol/m^3$   
 (= feed concentration to an incremental volume of the column)  
 $c_o$  = liquid bulk  $NO_x$  concentration (= 0  $mol/m^3$ )  
 $D$  = dispersion coefficient,  $m^2/s$   
 $d_p, d_p'$  = nominal packing diameter, m, ft  
 $D_v, D_v'$  = diffusivity,  $m^2/s, ft^2/hr$   
 $e'$  = operating void fraction  
 $e$  = dry bed void fraction  
 $E$  = enhancement factor  
 $Fr$  = Froude number  
 $G, G'$  = gas mass velocity,  $kg/m^2s, lb/ft^2hr$   
 $g$  = acceleration due to gravity,  $m/s^2$   
 $Ga$  = Galilei number  
 $ho, hs, ht$  = operating, static and total liquid holdup.  $m^3/m^3$   
 $j_D$  = mass transfer factor  
 $K$  = equilibrium constant,  $atm^{-1}$   
 $k_g'$  = gas phase mass transfer coefficient,  $lb\ mol/ft^2hr.atm$   
 $k_l$  = liquid phase mass transfer coefficient,  $mol/m^2s.atm$   
 $k_r$  = reaction rate constant  
 $L, L'$  = liquid mass velocity,  $kg/m^2s, lb/ft^2hr$   
 $M_m'$  = molecular weight of inert gas,  $lb/lb\ mol$   
 $p$  = partial pressure,  $atm., ppm$   
 $pe$  = Peclet number  
 $p_{Bm}$  = mean partial pressure of inert gas in the gas phase,  $atm., ppm$   
 $Re$  = Reynolds number  
 $T$  = absolute temperature, K  
 $u$  = velocity,  $m/s$

## Others

- $\rho$  = density,  $kg/m^3, lb/ft^3$   
 $\mu$  = viscosity,  $kg/m.s, lb/ft.hr$   
 $\sigma$  = surface tension, N/m

$$\text{Column absorption efficiency} = \frac{[NO_x]_{\text{absorbed}}}{[NO_x]_{\text{feed}}}$$

$$\text{Mean absorption rate} = \frac{1}{N} \sum_{i=0}^N E \cdot k_1 a \cdot (v_1 - c_o)$$

$$\text{Where } E = \frac{\sqrt{D_v k_r}}{k_1}$$

## Subscript

- $G$  = gas  
 $L$  = Liquid

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