Nitrogen Oxides Absorption into Sodium Hydroxide Solution in a
Packed Column Column: Effect of NaOH Concentration

by

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Abstract

Experiments have been conducted to evaluate the effect of sodium hydroxide (NaOH) concentration upon the absorption rate of nitrogen oxides (NOx) and packed column performance. The absorption process was carried out at atmospheric pressure and 298 K, using NaOH concentrations between zero and 19% w/w, NO/NO2 ratio of 0.5 and NOx concentrations between 150 and 10000 ppm in an air mixture.

The performance of the column was enhanced by the presence of hydroxyl ions (OH-) relative to the absorption into water, however, it was found to be independent of NaOH concentration. The absorption rate of NOx into NaOH solution was similar to that into water, suggesting that there is no direct reaction between NOx species and OH- ions, and thus in both cases, the absorption process was controlled by the hydrolysis of the main transporting species.

Column absorption efficiencies of about 92% and 87% were obtained during NOx absorption into NaOH and water, respectively.

Introduction

During simultaneous absorption of NO and NOx mixtures into aqueous solutions, it is believed that at higher NOx concentration (i.e. > 2000 ppm) the dissolution and hydrolysis of N2O3 are the major controlling mechanisms of absorption process[1-4] and below 2000 ppm the hydrolysis of NO2[5,6] and gas phase formation and physical absorption of HNO3[7,8] are the more predominant steps. However, it has been found that each reaction mechanism contributes significantly towards total absorption rate, at all NOx concentration levels.[6,7]

In the presence of OH- ions, the hydrolysis products are believed to be rapidly ionised and neutralized, so that any reversibility of the hydrolysis reactions is reduced or eliminated altogether. The decomposition of HNO3 is, however, believed to be fast enough to compete with the ionisation and neutralisation process.[10] If this happens it could result in NO formation which might diffuse out of the solution.[11,12] Komiyama and Inoue,[6] and Aoki et al[2] reported that OH ions prevent the HNO3 decomposition, thereby increasing the apparent absorption rate relative to similar absorption into water. They also reported that the rate of absorption does not vary with NaOH concentration for pH above 12.

Kameoka and Pigford[13] and Joshi et al, [3] however, reported that although the solubility and diffusivity of NOx decrease with increasing NaOH concentration, the hydrolysis rate constants of the same increase more strongly with NaOH concentration, so that the absorption rate increases with increasing NaOH concentration. They proposed the following absorption rate equations.

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\[ P_{\text{N}_{2}O_{4}} = \sqrt{D} k [H_2O] = K_1 [OH^-] P_{\text{N}_{2}O_{4}} \] (1)

\[ R_{\text{N}_{2}O_{3}} = \sqrt{D} k_2 [H_2O] + K_3 [OH^-] P_{\text{N}_{2}O_{3}} \] (2)

In light of this disagreement, the present experiments have been carried out to establish the effect of NaOH concentration upon the \( NO_x \) absorption rate and column performance.

**Theory**

The following equilibria and reactions take place during \( NO_x \) absorption into sodium hydroxide solution.\(^{1,6}\)

\[ 2NO_g + O_2g \leftrightarrow 2NO_{2g} \] (3)

\[ 2NO_{2g} \leftrightarrow N_2O_4g \] (4)

\[ NO_g + NO_{2g} \leftrightarrow N_2O_3g \] (5)

\[ NO_g \leftrightarrow NO_1 \] (6)

\[ NO_{2g} \leftrightarrow NO_{21} \] (7)

\[ N_2O_4g \leftrightarrow N_2O_{41} \] (8)

\[ N_2O_3g \leftrightarrow N_2O_{31} \] (9)

\[ 2NO_{21} \leftrightarrow N_2O_{41} \] (10)

\[ NO_1 + NO_{21} \leftrightarrow N_2O_{31} \] (11)

\[ N_2O_{41} + 2OH^- + (H_2O) \rightarrow NO_2^- + NO_3^- + H_2O \] (12)

\[ N_2O_{11} + 2OH^- + (H_2O) \rightarrow 2NO_2^- + H_2O \] (13)

\[ 2NO_{21} + 2OH^- + (H_2O) \rightarrow NO_2^- + NO_3^- + H_2O \] (14)

Also

\[ NO_g + NO_{2g} + H_2O_g \leftrightarrow 2HNO_{2g} \] (15)

\[ HNO_{3g} \leftrightarrow HNO_{21} \] (16)

\[ HNO_{21} + OH^- \rightarrow NO_2^- + H_2O \] (17)
The important NO\textsubscript{x} species in the gas phase include NO, NO\textsubscript{2}, NO\textsubscript{y}, N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O\textsubscript{5} and HNO\textsubscript{2}. The partial pressure of the effective nitrogen dioxide and nitric oxide, therefore may be defined as follows.\[^{14}\]

\[ P_{\text{eNO}} = P_{\text{NO}} + 2P_{\text{N2O4}} + P_{\text{N2O3}} + \frac{1}{2} P_{\text{HNO2}} \]  \hspace{1cm} (18)

and

\[ P_{\text{eNO}} = P_{\text{NO}} + P_{\text{N2O3}} + \frac{1}{2} P_{\text{HNO2}} \]  \hspace{1cm} (19)

The concentration of different species can be calculated by assuming the above equilibria to be fully established, thus:

\[ P_{\text{N2O4}} = K_1 P_{\text{NO}}^2 \]  \hspace{1cm} (20)

\[ P_{\text{N2O3}} = K_2 P_{\text{NO}} P_{\text{NO2}} \]  \hspace{1cm} (21)

\[ P_{\text{HNO2}} = \sqrt{K_3 P_{\text{NO}}^2 P_{\text{NO2}}^2 P_{\text{H2O}}} \]  \hspace{1cm} (22)

The absorption into NaOH at all NO\textsubscript{x} concentrations was assumed to be controlled by pseudo first order hydrolysis of N\textsubscript{2}O\textsubscript{y}, pseudo second order hydrolysis of NO\textsubscript{2}, gas phase formation and physical absorption of HNO\textsubscript{2} and physical absorption of NO and NO\textsubscript{x}. Also partial oxidation of NO was assumed to be present.\[^{6}\]

The mass balance across a differential volume of the column yields

\[ G(C_{6\text{in}} - C_{6\text{out}}) = a A R_e \Delta h \]  \hspace{1cm} (23)

\[ \lim_{\Delta h \to 0} \frac{(C_{6\text{in}} - C_{6\text{out}})}{\Delta h} = \frac{dC_6}{dh} = \frac{aA}{G} R_e \]  \hspace{1cm} (24)

\[ \int_{C_{6,\text{in}}}^{C_{6,\text{out}}} \frac{dC_6}{R_e} = \frac{aA}{G} \int_{h=0}^{h=H} dh \]  \hspace{1cm} (25)

Where

\[ R_e = R_{\text{eNO2}} + R_{\text{eNO}} \]  \hspace{1cm} (26)

\[ R_{\text{eNO2}} = R_2 + 2R_4 + R_3 + \frac{1}{2} R_5 + R_2' - R_3' \]  \hspace{1cm} (27)

\[ R_{\text{eNO}} = R_3 + \frac{1}{2} R_5 + R_4 \]  \hspace{1cm} (28)

From the two film absorption theory, the general equation for a pseudo n\textsuperscript{th} order reaction is given by the following equation.\[^{15}\]

Therefore,

\[ R_4 = \frac{1}{R_4 V (K_d)_d P_3} \]  \hspace{1cm} (30)
\[
R_x = \sqrt{\frac{2}{n+1} D_x k_x (\bar{H}_x P_x)^{n+1/2}}
\]

(29)

\[
R_1 = \bar{H}_1 \sqrt{(kD)_1 P_1}
\]

(31)

\[
R_2 = \sqrt{\frac{2}{3} k_2 D_2 (\bar{H}_2 P_2)^{1.5}}
\]

(32)

And

\[
R'_1 = k_1 \bar{H}_1 P_1
\]

(33)

\[
R_{HNO_2} = k_3 \sqrt{K_{p_1} P_1 P_2 P_{HNO_2}}
\]

(34)

\[
R_1 = k_1 \bar{H}_1 P_1
\]

(35)

\[
R'_1 = k_1 P_1^2 P_{O_2}
\]

(36)

Table 1 shows the parameters used to make model predictions for various absorption conditions present.\(^{(6)}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Ref. Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\bar{H}/(kD))_{N_2O_4})</td>
<td>0.116</td>
<td>m/s</td>
<td>6</td>
</tr>
<tr>
<td>((\bar{H}/(kD))_{N_2O_3})</td>
<td>2.721</td>
<td>m/s</td>
<td>6</td>
</tr>
<tr>
<td>(k_1)</td>
<td>2.1E-2</td>
<td>m/s</td>
<td>7</td>
</tr>
<tr>
<td>(k_2)</td>
<td>3.75E-5</td>
<td>m/s</td>
<td>7</td>
</tr>
<tr>
<td>(K_1)</td>
<td>6.86</td>
<td>atm(^{-1})</td>
<td>16</td>
</tr>
<tr>
<td>(K_2)</td>
<td>0.535</td>
<td>atm(^{-1})</td>
<td>16</td>
</tr>
<tr>
<td>(k_3)</td>
<td>1.01</td>
<td>atm(^{-1})</td>
<td>16</td>
</tr>
<tr>
<td>(k_4)</td>
<td>2.62E-11</td>
<td>ppm(^2)s(^{-1})</td>
<td>17</td>
</tr>
<tr>
<td>(H_1)</td>
<td>1.2E-2</td>
<td>kmol/m(^3)atm</td>
<td>16</td>
</tr>
<tr>
<td>(H_2)</td>
<td>1.93E-3</td>
<td>kmol/m(^3)atm</td>
<td>16</td>
</tr>
<tr>
<td>(a)</td>
<td>157</td>
<td>1/m</td>
<td>7</td>
</tr>
<tr>
<td>(k_2)</td>
<td>2.1E7</td>
<td>m(^3)/kmol.s</td>
<td>16</td>
</tr>
<tr>
<td>(D_2)</td>
<td>1.8E-9</td>
<td>m/s</td>
<td>16</td>
</tr>
<tr>
<td>(P_{O_2})</td>
<td>2.1E5</td>
<td>ppm</td>
<td>(% O(_2) in air)</td>
</tr>
<tr>
<td>(P_{N_2O_3})</td>
<td>2.0E4</td>
<td>ppm</td>
<td>(thermodynamic tables)</td>
</tr>
</tbody>
</table>

**Experimental Apparatus and Procedure**

A schematic diagram of the experimental equipment is shown in Figure 1. It consisted of a 7.75 cm i.d. glass column, packed with 1.25 cm (diameter x length) 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 plug flow was approached closely.\(^{(19)}\) The absorption of NO\(_x\) gas (NO/NO\(_x\) = 0.5) was performed at atmospheric pressure, 298 K and constant liquid and gas flow rates, of 0.8 and 40 l/min,
respectively. The NaOH concentration was varied from zero to 19\% w/w. The liquid and gas streams were manually controlled with the aid of floatmeters to the top and bottom of the column, respectively. The feed and effluent gaseous NO\(_x\) concentrations were measured by a chemiluminescent gas NO\(_x\)/NO analyser (Grubb Parson Chemitox). The NaOH concentration was monitored by a standard titrimetric method.

Results and Discussion

The application of the model to predict the NO\(_x\) absorption rate and column absorption efficiency is reported in a separate paper.\(^{[6]}\)

Figure 2 shows the plot of the relative column absorption efficiency using water and NaOH solution (5.88\% w/w). The column absorption efficiency is defined as follows.

\[
\eta = \frac{[\text{NO}_x]_{\text{absorbed}}}{[\text{NO}_x]_{\text{in}}} \tag{37}
\]

![Figure 2](image_url)

![Figure 3](image_url)

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It can be seen that there is about 5% increase in absorption efficiency in favour of absorption into NaOH solution. This increase can be attributed to the substitution of HNO₃ decomposition, which tends to increase the NO₂ concentration in the outlet stream, by neutralisation. This explanation is supported by the results shown in Figure 3, which depicts the relative absorption efficiency of NO₂⁻ (NO₂⁻ = NO₂ + 2N₂O₂) into water and NaOH solution in the same column. During NO₂⁻ absorption into water the absorption efficiency increases with increasing NO₂⁻ concentrations up to 2500 ppm, then it start falling with a further increase in NO₂⁻ concentration.

During NO₂⁻ absorption the hydrolysis products are both HNO₃ and HNO₂, whereas HNO₂ is the predominant product during NO₂ absorption. The HNO₂ can decompose in the liquid phase according to the following reaction mechanism.

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$ (38)

This means, when absorbing NO₂⁻, the neutralisation of the hydrolysis products, or the diffusion and decomposition of HNO₂ with associated formation and desorption of NO, accelerate the formation and dissolution of more N₂O₃ and HNO₂ so that the column absorption efficiency increase with increasing NO₂⁻ concentration for both NaOH and water absorbants. But the decomposition of HNO₂ and subsequent accumulation of free HNO₃, locally reduces the rate of hydrolysis of N₂O₃ and the column absorption efficiency when water is used as absorbant. Since the NO in the outlet stream was always smaller than that in the inlet stream, it was not possible to tell whether the NO in the outlet was "unreacted portion" of the inlet NO or was formed within the column as a result of HNO₂ decomposition. The absorption of NO₂⁻ into water, however, revealed that at least part of NO was formed within the column (since the NO was present in the outlet stream and its concentration increased with NO₂⁻ concentration) suggesting the presence of HNO₂ decomposition in the absence of OH⁻ radicals.

The formation of HNO₃, locally reduces the rate of hydrolysis of N₂O₃ so that the building up of free HNO₃ decreases the rate of uptake of NO₂⁻ (according to Le Chatelier's principle). At low NO₂⁻ concentrations (< 2500 ppm) the HNO₂ formed is far below its pseudo steady state equilibrium concentration, at which it decomposes steadily, thus the NO₂⁻ flux and column absorption efficiency will appear to increase with increasing mass transfer driving force (ie NO₂⁻ concentration). It is worth mentioning that in the absence of HNO₂ decomposition the column absorption efficiency is higher when water is used as absorbant. this is probably due to the fact that the solubility and diffusivity of NO₂⁻ species are lower in concentrated NaOH than in water, see Table II.

Nevertheless, it can be seen from Figure 2 that the column absorption efficiency is a strongly dependent upon the NO₂ absorbant concentration. The absorption efficiencies of up to 92% and 87% were obtained during 10000 ppm NO₂ absorption into NaOH and water, respectively.
Figure 4 shows that the column absorption efficiency is always higher into NaOH than into water as long as there is enough OH⁻ ion present to neutralise the hydrolysis products. The absorption efficiency does not vary with varying NaOH concentration when this concentration is between 3.7 and 11.2% w/w. Above 11.2% w/w the absorption efficiency decreases slightly with increasing NaOH concentration. This can be attributed to the increasing viscosity and decreasing activity coefficient of NaOH solution and a decrease in the solubility and diffusivity of NO₂ species with increasing NaOH concentration. It is also worth mentioning that the water vapour pressure decreases with increasing NaOH concentration, which might reduced the contribution due to gas phase formation and absorption of HNO₂ and hence the column performance.

The column absorption efficiency and NO₂ absorption rate for the lower range of NO₂ concentrations (below 5000 ppm) into water are higher than into a 0.13% NaOH solution, as shown in Figures 4 and 5, respectively. This can be attributed to the slow transportation of OH⁻ ions due to the reduced driving force and a slight decrease of the activity coefficient of NaOH solution, the diffusivity and solubility of NO₂ species and to a slight increase in the viscosity of the solution, see Table ii. The absorption rate into water and 0.13% NaOH is, however, almost the same when absorbing from 10000 ppm NO₂. This can be explained by the fact that the decomposition of HNO₂ is probably occurring very close to the liquid surface and at the same rate in both water and dilute NaOH.
Table II: Comparison of physical properties of the absorbants of the absorbants and NO\textsubscript{x} species into water and NaOH solution.

<table>
<thead>
<tr>
<th>Species</th>
<th>Water</th>
<th>NaOH Solution (0.13%)</th>
<th>Units</th>
<th>Increase or Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>-</td>
<td>1.0E-3</td>
<td>1.005E-3</td>
<td>NS/m\textsuperscript{3}</td>
</tr>
<tr>
<td>Activity</td>
<td>-</td>
<td>1.00</td>
<td>0.792</td>
<td>-</td>
</tr>
<tr>
<td>Solubility</td>
<td>N\textsubscript{2}O\textsubscript{4}</td>
<td>1.5</td>
<td>1.493</td>
<td>kmol/m\textsuperscript{3} atm</td>
</tr>
<tr>
<td></td>
<td>N\textsubscript{2}O\textsubscript{3}</td>
<td>0.7</td>
<td>0.690</td>
<td>kmol/m\textsuperscript{3} atm</td>
</tr>
<tr>
<td></td>
<td>NO\textsubscript{2}</td>
<td>1.7E-2</td>
<td>1.47E-2</td>
<td>kmol/m\textsuperscript{3} atm</td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>1.9E-3</td>
<td>1.67E-3</td>
<td>kmol/m\textsuperscript{3} atm</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>All</td>
<td>-</td>
<td>-</td>
<td>m\textsuperscript{2}/s</td>
</tr>
</tbody>
</table>

Figure 6 shows the variation of mean surface absorption rate with NaOH concentration. Obviously, there is no apparent dependence of the NO\textsubscript{x} absorption rate upon the NaOH concentration. This confirms the fact that there is no direct reaction between OH\textsuperscript{-} ions and NO\textsubscript{x} species. The observed increase in absorption efficiency is, therefore, due to neutralisation of the hydrolysis products. The solid line represents the model predictions which are in good agreement with experimental data, and thus the model can be used to predict the absorption rate for various NaOH concentrations without modifying the value of the absorption coefficients ($\bar{H}/(kD)$).

![Figure 6 Effect of NaOH Concentration on NO\textsubscript{x} Absorption Rate](image-url)
Conclusion

The experimental investigation shows no evidence of direct reaction between $\text{OH}^-$ ions and $\text{NO}_x$ species. The increase in the column absorption efficiency into NaOH solution relative to that into water can be attributed to the neutralization of the hydrolysis products. This phenomenon eliminates secondary formation of NO, which otherwise would increase the amount of NO in the outlet stream, and also enhances the hydrolysis of more NO$_2$ by removing HNO$_2$. The reduction in mean absorption into dilute NaOH solution is most probably due to the slower transportation of $\text{OH}^-$ ions from the liquid bulk to the interface as a result of the reduced driving force now available.

Good agreement between the model predictions and experimental data confirms that the primary $\text{NO}_x$ absorption mechanisms are absorption in the presence of fast pseudo-first order hydrolysis of N$_2$O$_3$ and N$_2$O$_4$, slow pseudo-second order hydrolysis of NO and gas phase resistance controlled dissolution and reaction of HNO$_2$ vapour formed by a homogeneous gas phase reaction.

Nomenclature

\begin{align*}
a & = \text{gas liquid interfacial area, m}^2/\text{m}^3 \\
c_i & = \text{species concentration, mol/ m}^3 \\
d & = \text{diffusion coefficient for species i, m}^2/\text{s} \\
e\text{NO}_3 & = \text{effective nitrogen dioxide} \\
e\text{NO}_\text{aq} & = \text{effective nitric oxide} \\
g & = \text{gas flow rate, m}^3/\text{s} \\
h & = \text{solubility constant, kmol/m}^3/\text{atm} \\
k_{ps} & = \text{gas side mass transfer coefficient, m/s} \\
k_{lp} & = \text{liquid side mass transfer coefficient, m/s} \\
k & = \text{equilibrium constant for reaction, atm}^{-1} \\
r & = \text{reaction rate constant, m}^3/\text{kmol.s} \\
r & = \text{absorption rate, mol/m}^2\text{s} \\
R & = \text{amount of NO}_x \text{absorbed divided by the total area}
\end{align*}

Subscripts

1 = NO \\
2 = NO$_2$ \\
3 = N$_2$O$_3$ \\
4 = N$_2$O$_4$ \\
5 = HNO$_2$ \\
6 = NO$_x$

References.


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