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# Absorptive $NO_x$-Reduction

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# ABSORPTIVE $NO_X$ -REDUCTION

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## ABSTRACT

Absorptive reduction of NO-from off-gas has been investigated. With regard to negligibly low solubility of nitrogen monoxide in aqueous solutions, technical application of any absorption process has to be based on absorption with chemical reaction at the interphase. The present investigations have been based on the redox reaction

$$2\,NO + 4\,H^{+} + 4\,e^{-} \Rightarrow N_2 + 2\,H_2O$$

Combining this thermodynamic principle of NO-reduction with a redox-absorption process should enable separation processes comparable with SCR-denoxing. Several processes with promising redox conditions have been investigated. The program has considered the reactivity, the nature of products and mass transfer problems. The results confirm, that NO itself does not participate any kind of reactive absorption process. Nitrogen monoxide has to be preferably oxidized in a first step to form $NO_2$ and has to be absorbed in a second step. Depending on the ratio of $NO/NO_2$ (or $NO/N_2O_4$) the products may differ. Gaseous $N_2$ has definitely been observed only, when absorbing $NO_2/N_2O_4$.

## INTRODUCTION

In denoxing, physical absorption processes suffer from negligible efficiency. Enhancement by the use of complexing agents has been reported. Iron(II) compounds are well-known complexing agents (1-9). But their effect on NO-separation is beyond technical demand. Besides, their chemical stability is low. As a matter of fact selective catalytic reduction (SCR) is still the only process which has gained technical application in the

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denoxing of off-gas. But off-gas in different processes, mainly incineration processes applied in waste management, may cause a rapid loss of activity of the catalysts used in denoxing processes.

Technical application of the absorptive removal of nitrogen monoxide from off-gas demands either oxidation or reduction of the species within the separation process. The chemical fundamentals and the basic mass transfer problems of several absorption processes have been investigated. The objective of the program has been the evaluation of methods for absorptive $NO_x$-removal from off-gas and the investigation of processes of technical interest. Nitrogen monoxide has mainly been considered.

## FUNDAMENTALS OF $NO_X$-FORMATION

Before dealing with absorptive methods a brief summary of gaseous and gas/liquid interactions of NO will be discussed.

The main $NO_x$ gases are NO, $NO_2$, $N_2O_3$ and $N_2O_4$. The very low solubility of NO in water ($H_{298K}$=28,000 bar) (10) does not enable absorptive separation. The higher nitrogen oxides $NO_2$, $N_2O_3$ and $N_2O_4$ show a better solubility in water. Following reactions may occur in the gaseous phase (11):

$$2\,NO(g) + O_2 \Rightarrow 2\,NO_2\,(g) \qquad (1)$$

$$2\,NO_2\,(g) \Leftrightarrow N_2O_4\,(g) \qquad (2)$$

$$NO\,(g) + NO_2\,(g) \Leftrightarrow N_2O_3\,(g) \qquad (3)$$

$$NO\,(g) + NO_2\,(g) + H_2O\,(g) \Leftrightarrow 2\,HNO_2\,(g) \qquad (4)$$

Oxidation of NO to $NO_2$ is a third order reaction (second order with regard to NO) (12,13) and the $NO_2$-concentration (% by volume) can be calculated with equation 5 when using air as carrier. The parameter $t_R$ (s) represents the reaction time.

$$[NO_2] = \frac{k_2 * t_R * [NO]^2}{1 + k_2 * t_R * [NO]} \qquad (5)$$

The rate constant $k_2$ ($\%^{-1} * s^{-1}$) of the experimental data (13) can be expressed by equation 6:

$$k_2 = 0.062 * \exp(-0.011 * T) \tag{6}$$

Nitrogen dioxide and the dimer $N_2O_4$ form an instant equilibrium (11,13). The rate constant $K_{G1}$ $(kN/m^2)^{-1}$ of equation 2 is given by the expression:

$$\log_{10} K_{G1} = \frac{2993}{T} - 11.232 \qquad \text{with } K_{G1} = \frac{pN_2O_4}{p^2 NO_2} \tag{7}$$

Figure 1 shows the temperature dependency of equation 7. If the content of $NO_2$ is less than 100 ppmv, the formation of $N_2O_4$ is negligible ($\leq 0.5\%$). Both oxides ($NO_2$ and $N_2O_4$) are soluble in water, but the Henry coefficient of the dimer $N_2O_4$ is 100 times smaller with water than the Henry coefficient of $NO_2$ (10). Both oxides react equimolar by forming nitrous and nitric acid. As known from nitric acid production, nitrous acid decomposes to nitric acid and NO, which desorbs into the gaseous phase. Further, mixtures of NO and $NO_2$ react to $N_2O_3$ corresponding to equation 3. The rate constant $K_{G2}$ $(kN/m^2)^{-1}$ of the formation of $N_2O_3$ corresponds with the expression below (11):

$$\log_{10} K_{G2} = \frac{2072}{T} - 9.24 \qquad K_{G2} = \frac{pN_2O_3}{pNO * pNO_2} \tag{8}$$

Figure 2 shows the formation of $N_2O_3$ with varying $NO_x$-concentration. A maximum of $N_2O_3$ is formed at an equimolar ratio of $NO/NO_2$ (see equation 8). In spite of the optimum ratio of $NO/NO_2$,the formation of $N_2O_3$ decreases with $NO_x$-contents of less than 1000 ppmv ($NO + NO_2$).

$NO_2$, $N_2O_3$ and $N_2O_4$ react with water. Therefore no direct measurement of the Henry coefficient is possible. An estimation of Henry coefficients,represented in table 1, is based on liquid phase equilibria, kinetic studies and physical properties (10).

## STATE OF THE ART AND FIELD OF INVESTIGATION

The technological pathways of the absorptive removal of nitrogen monoxide may be classified by the groups listed below:

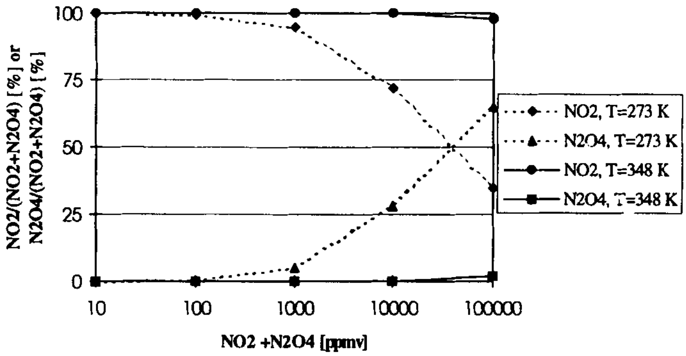

FIGURE 1. Gaseous phase equilibrium of $NO_2/N_2O_4$ in the temperature range of 273-348 K ($NO_x$ describes either $NO_2$ or $N_2O_4$)

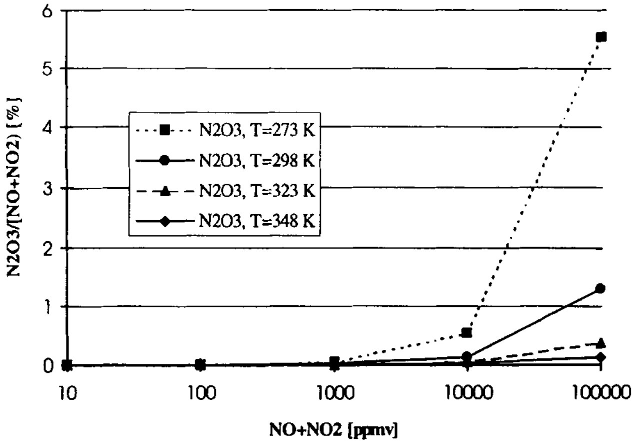

FIGURE 2. Gaseous phase equilibrium of $N_2O_3$ in the temperature range of 273-348 K; ratio of $NO/NO_2$ = 1

TABLE 1. HENRY COEFFICIENTS OF NO, $NO_2$, $N_2O_3$ AND $N_2O_4$, T=298 K

| | *H [M*atm]* | *H [bar]* |
|---|---|---|
| NO | $1.93*10^{-3}$ | 28,400 |
| $N_2O_3$ | $0.6\pm0.2$ | $92.6\pm^{46.3}_{23.1}$ |
| $NO_2$ | $1.2\pm0.4*10^{-2}$ | $4,630\pm^{2,315}_{1,160}$ |
| $N_2O_4$ | $1.4\pm0.7$ | $39.7\pm^{39.7}_{13.5}$ |

### Oxidation-Absorption Processes

This process has become known by the synonym Walther-process (14). It was initially published in the eighties and was thought to combine pollution control with the recovery of the fertilizer ammonium nitrate. In a first step, NO was oxidized in the gaseous phase by ozone to form $NO_2$ and the dimer $N_2O_4$. In a second step these substances were absorbed in aqueous ammonia by forming the nitrite and the nitrate of ammonia. Both the enormous cost for the production of ozone and the low efficiency in products limited the practical application.

### Absorption-Oxidation Processes

In the presence of strong oxidizers ($KMnO_4$, $K_2Cr_2O_7$, $NaClO_2$ etc.), the aqueous solution of NO and its derivates ($NO_2$, $N_2O_3$ and $N_2O_4$) will be oxidized by forming nitrate (8, 11). As oxidation takes place in the aqueous phase, the process is limited by the mass transfer conditions for the substance NO from the gaseous to the liquid phase. Finally the products do have a low level of quality and demand a lot of purification (31). These processes are therefore very expensive.

### Absorption-Reduction Processes

Compared with the absorption techniques mentioned above, the absorption-reduction process works on the chemical principle of nitrogen formation from $NO_x$. In case of NO-absorption,the process corresponds with the basic thermodynamic reactions (15):

$N_2O + 2\,H^+ + 2\,e^- \Leftrightarrow N_2 + H_2O \qquad E_0 = +\,1.77\ V \qquad (9)$

$2\,NO + 2\,H^+ + 2\,e^- \Leftrightarrow N_2O + H_2O \qquad E_0 = +\,1.59\ V \qquad (10)$

$2\,NO + 4\,H^+ + 4\,e^- \Leftrightarrow N_2 + 2\,H_2O \qquad E_0 = +\,1.68\ V \qquad (11)$

The process should not cause any by-products or residues and it should therefore be comparable with the process of selective catalytic reduction. Actually the basic reaction is an ideal boundary as several by-products will be formed under given conditions of operation.

Within this program several techniques and additives have been investigated. For comparison, the program was started with mass transfer experiments using iron(II) containing solvents. Literature reports improvement in the efficiency of absorption of $NO_x$ when iron(II) containing solvents are applied at elevated pH-values and low oxygen content of the off-gas (1-8).

The effect of $SO_2$ on the efficiency of $NO_x$-absorption by Fe(II) does have a high degree of technical interest. But this process must be operated under alkaline conditions(11, 16-19)

Compared with the separation of NO by the formation of nitrosyls the efficiency of reduction of NO to nitrogen is negligible (20). But in comparison, the $NO_x$-separation based on the reduction of $NO_2$ by the solvent or in the solvent is of technical interest. Summing up these boundaries therefore means that pretreatment of the gaseous phase by oxidizing NO to form $NO_2/N_2O_4$ is necessary.

Table 2 represents the qualitative evaluation of additives, which have been investigated during the program. As shown by the results, the reduction of NO has only been observed when the system Fe(II)/$SO_2$ was applied. But several additives do react with $NO_2$ and they do preferably cause the formation of nitrogen.

## EXPERIMENTAL SET UP

This investigation of absorptive $NO_x$-removal has led into two directions. On one hand, the mechanism of absorption and formation of products has been investigated. On

TABLE 2. REACTIVE ADDITIVES USED FOR $NO_X$-ABSORPTION

| *reactive additive* | *NO-absorption* | *$NO_2$-absorption* | *$NO_x$-absorption* |
|---|---|---|---|
| water (11) | - | + | - |
| 0.23 M hydroquinone, acidified with 2 M $H_2SO_4$ (28) | - | ++ | - |
| 0.5 M oxalic acid (28) | - | + | - |
| 1 M diamide (28) | - | ++ | ++ |
| Cr(II)/Cr(III)-system (21) | - | + | + |
| urea (11, 29) | - | + | - |
| sulfanilic acid (25) | - | + | + |
| 0.25 M $NaSO_3$ (30) | - | + | + |
| acidified $FeSO_4$ + simultaneous $SO_2$-absorption (11) | + | + | + |
| 0.04 M morpholine (28) | - | + | + |

| | |
|---|---|
| - : | no absorption occurs with the reactive solvent |
| + : | ≤ 50 % of $NO_x$-absorption occurs in an impinging system |
| ++: | > 50 % of $NO_x$-absorption occurs in an impinging system |

the other hand mass transfer data have been evaluated. Both have been carried out in lab scale testing equipment.

Before carrying out the experiments, the equipment was calibrated with the test system $SO_2$/air/solvent.

## Equipment used for Testing the Chemistry and Mechanism of $NO_x$-Absorption

Mechanism and formation of products have been investigated in an impinger, which is comparable with a foam scrubber.

The test-gas used in the experiments has been prepared by mixing air or nitrogen with NO and/or $NO_2$ (respectively $SO_2$ for calibrating the impinger). The flow rate of both gases has been controlled by thermoanemometric regulation (RV1, RV2). The $NO_x$-content has been measured by chemiluminescence detection, the $SO_2$ and $N_2O$-content by non dispersive infrared detection. Figure 3 shows the principal flowchart of the experimental set-up.

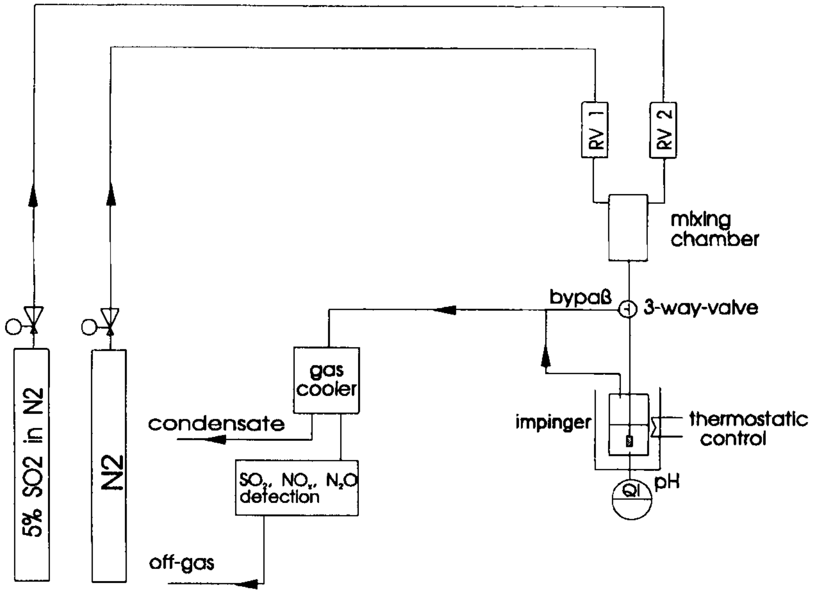
RV 1
RV 2
mixing chamber
bypaß
3-way-valve
gas cooler
condensate
impinger
thermostatic control
SO$_2$, NO$_x$, N$_2$O detection
QI
pH
off-gas
5% SO2 in N2
N2

FIGURE 3. Flowchart of the experimental set-up used for investigating the mechanismn of NO$_x$-absorption

### Equipment used for Testing the Mass Transfer in NO$_x$-Absorption

Mass transfer data were determined through experiments in a film absorptive column. The film absorber is designed as a concentric tube apparatus (figure 4).

The size of the film absorber is 2.13 m in active height, an inner diameter of 33.4 mm and an outer diameter of 49.5 mm of the concentric annular gap.

The solvent, stored in a tank, is pumped to the top of the column and is distributed on top of the inner tube. At the bottom of the film absorber, drillings in the inner tube enable the draining of the solvent.

The test gas has been prepared by mixing compressed air with NO$_2$ (SO$_2$ for calibration of the film column). Pressure and temperature control permits evaluation of the standard flow rate. The gas enters the column at the bottom and moves up the concentric annular gap. At the bottom and at the top of the column, on-line measurement of the gaseous phase enables integral analysis of the experimental results.

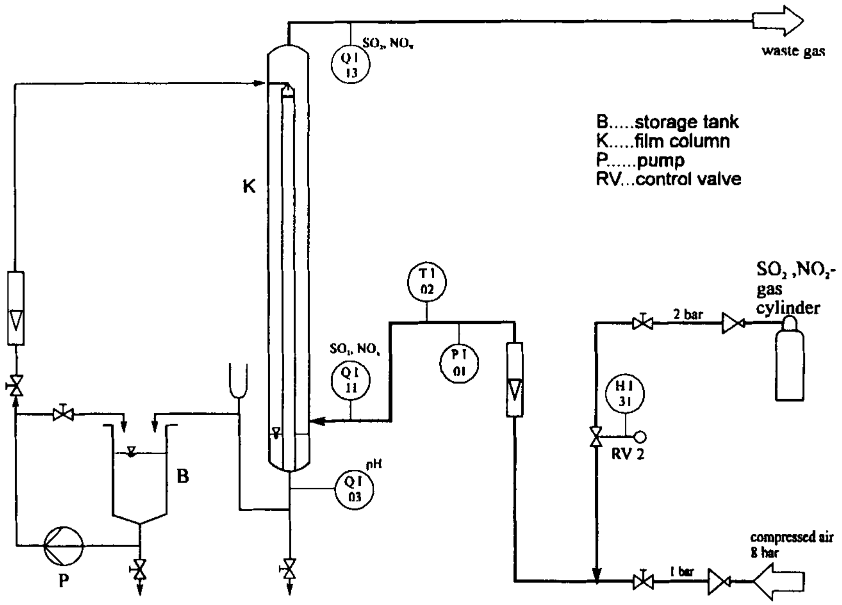
SO$_2$, NO$_x$
QI 13
waste gas
B.....storage tank
K.....film column
P......pump
RV...control valve
K
TI 02
SO$_2$, NO$_2$-gas cylinder
2 bar
SO$_2$, NO$_x$
QI 11
PI 01
HI 31
RV 2
B
pH
QI 03
compressed air 8 bar
1 bar
P

FIGURE 4. Flowchart of the experimental set-up used for investigating the mass transfer of NO$_x$-absorption

## CALIBRATION OF THE EXPERIMENTAL SET-UP

### Calibration of the Equilibrium Equipment

The performance of the absorption device was tested with the test system SO$_2$/air/solvent. This absorption process may be observed to be controlled by the gas phase resistance, as shown by equations 12 to 15. Chemical boundaries of the test system at 25°C are (21):

$$SO_2\,(g) \Leftrightarrow SO_2\,(aqu.) \qquad pK_{HS} = -0.134 \qquad (12)$$

$$SO_2\,(aqu.) + 2\,H_2O \Leftrightarrow H_3O^+ + HSO_3^- \qquad pK_{S1} = 1.96 \qquad (13)$$

$$HSO_3^- + H_2O \Leftrightarrow H_3O^+ + SO_3^{2-} \qquad pK_{S2} = 7.0 \qquad (14)$$

$$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^- \qquad pK_w = 14.0 \qquad (15)$$

Under consideration of electroneutrality, the vapor pressure of $SO_2$ may be correlated with the pH-value according to equation 16:

$$c_{H^+} = c_{OH^-} + c_{HSO_3^-} + 2c_{SO_3^{2-}} \tag{16}$$

In accordance with equation 16, the vapor pressure of $SO_2$ is negligible at elevated pH-values and at equilibrium with an aqueous phase, as demonstrated by figure 5.

As shown by figure 5, the vapor pressure for $SO_2$ of an aqueous solution is less than 1 ppmv at pH-values above 6.3. The gaseous concentration of $SO_2$ at the interphase may therefore be assumed to be negligible too. Under these conditions mass transfer is assumed to be controlled by the transport of $SO_2$ from the gaseous bulk phase to the interphase.

The calibration tests were therefore carried out with an aqueous solution of sodium hydroxide. Based on the chemical fundamentals represented by equation 16, the experimentally obtained content of $SO_2$ in the off-gas of the test unit was negligible even at very high $SO_2$-contents in the feed-gas of 4000 mg $SO_2/m^3$.

On account of these results, the investigation of the chemistry of $NO_x$-absorption in the described test unit may be based on the fact that it is possible to achieve equilibrium conditions in the calibrated impinger test unit.

## Calibration of the Mass Transfer Equipment

According to the calibration of the impinger, the calibration tests were carried out with the calibration gas $SO_2$ and the solvent sodium hydroxide again. Table 3 shows the experimentally obtained data for the film column (T=298 K).

The experiments were compared by the HTU-NTU-concept which describes the height of the absorber. As mentioned the concentration of $SO_2$ is negligible at elevated pH-values. The concentration of $SO_2$ at the interphase is then assumed to be zero and the NTU-value (number of transfer units) is correlated by equation (17).

$$NTU_g = \int \frac{dc}{c - c_I} = \ln \frac{c_{bottom}}{c_{top}} \tag{17}$$

The height of the transfer unit (HTU) is given by following equation:

$$HTU_g = \frac{\dot{G}}{\beta_g * a * S} \tag{18}$$

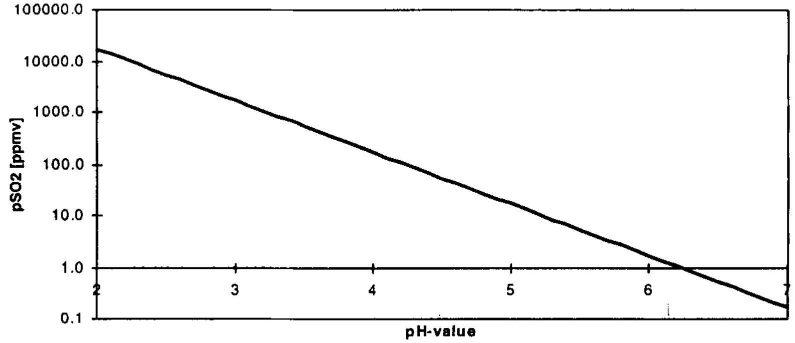

FIGURE 5. Correlation of the maximum content of $SO_2$ in the gaseous phase at equilibrium with an aqueous phase and at different pH-values

TABLE 3: $SO_2$-CONTENT AT THE BOTTOM AND AT THE TOP OF THE ABSORBER

| *solvent [l/h]* | *G [$m^3/h$]* | *wg [m/s]* | $c_{bottom}$ *[$mg/m^3$]* | $c_{top}$ *[$mg/m^3$]* |
|---|---|---|---|---|
| 20 | 3.3 | 0.9 | 982 | 305 |
| 20 | 5.6 | 1.5 | 995 | 344 |
| 20 | 7.8 | 2.0 | 1004 | 376 |
| 20 | 10.0 | 2.6 | 1004 | 388 |
| 20 | 12.2 | 3.2 | 995 | 396 |
| 40 | 3.3 | 0.9 | 1018 | 312 |
| 40 | 5.6 | 1.5 | 1010 | 338 |
| 40 | 7.8 | 2.0 | 1002 | 359 |
| 40 | 10.0 | 2.6 | 993 | 372 |
| 40 | 12.2 | 3.2 | 998 | 382 |
| 60 | 3.3 | 0.9 | 992 | 298 |
| 60 | 5.6 | 1.5 | 1010 | 323 |
| 60 | 7.8 | 2.0 | 995 | 345 |
| 60 | 10.0 | 2.6 | 988 | 358 |
| 60 | 12.2 | 3.2 | 1002 | 371 |

The height of the absorber can be calculated with equation (19) if the gaseous mass transfer coefficient $\beta_g$ is known. Choosing an appropriate mass transfer model enables the interpretation of the experimental data and the comparison with the actual absorber height.

$$H = HTU * NTU \qquad (19)$$

As reported in literature, equations 20-22 describe the mass transfer from the gaseous bulk phase to the interphase of a film absorber (22). The region of validity is between $2{,}000 \leq Re_g \leq 35{,}000$ with $w_g$ being the dry gas velocity.

$$Sh_g = 0.023 * Re_g^{0.83} * Sc_g^{0.44} \qquad (20)$$

$$Re_g = \frac{w_g * d}{\nu_g} \qquad (21)$$

$$Sc_g = \frac{\nu_g}{D_g} \qquad (22)$$

The calculation of the liquid phase mass transfer is described by equation 23-28:

$$Sh_l = 1.39 * Re_l^{0.33} * Sc_l^{0.5} * Ga^{0.167} * \Gamma^{-0.5} \qquad (23)$$

$$Re_l = \frac{w_l * d_{hydr}}{\nu_l} \qquad (24)$$

$$Ga = \frac{g * d_{hydr}^{3}}{\nu_l^{2}} \qquad (25)$$

$$\Gamma = \frac{H}{d} \qquad (26)$$

The hydraulic diameter $d_{hydr}$ and the film thickness correlate with equation 27:

$$d_{hydr} = 4 * f \qquad (27)$$

The film thickness is calculated from the volume flow rate of the solvent by equation 28 (validity range $Re_l \leq 1600$ (23)).

$$\dot{L} = d * \pi * \frac{g * f^{3}}{3 * \nu_l} \qquad (28)$$

Comparing the experimental data with mass transfer models from literature shows good accordance for gaseous phase controlled mass transfer (Figure 6).

## RESULTS AND DISCUSSION

According to table 2 several additives were investigated. As mentioned, different gas mixtures, including $NO/N_2$, $NO_2/N_2$, $NO_x/N_2$, NO/air, $NO_2$/air and $NO_x$/air, were used. In general, the investigation concentrated on the absorption of NO. The results are discussed below.

### Test of the Solvent Water

Absorption of NO in water is determined by a very low solubility. As reported elsewhere (10), the Henry coefficient of NO is H = 28,000 bar at a temperature of 298 K. Absorption of $NO_2$ takes place more readily. The degree of absorption depends on the $NO_2$-content in the gaseous phase (11). Synergetic effects on the coabsorption of NO have not been detected. Figure 7 shows the various mechanism of $NO_x$-absorption in water.

### Test of the Redox-additives Hydroquinone and Oxalic Acid

Based on the fundamental thermodynamic equation of NO-reduction (15), the absorptive removal of nitrogen monoxide should be possible with the redox-system hydroquinone/quinone in accordance with following mechanism:

$$2\,NO + 4\,H^+ + 4\,e^- \Rightarrow N_2 + 2\,H_2O \qquad E_0 = +\,1.68\ V \qquad (29)$$

$$\text{hydroquinone} \Leftrightarrow \text{quinone} + 2\,H^+ + 2\,e^- \qquad E_0 = +\,0.70\ V \qquad (30)$$

Experimental tests in the impinger showed that NO cannot be absorbed under these conditions. $NO_2$ seems to be absorbed quantitatively. But detection shows that $NO_2$ is quantitatively transfered into NO by oxidizing hydroquinone to quinone. Similar results were achieved when testing oxalic acid, which has better reducing properties in comparison with hydroquinone.

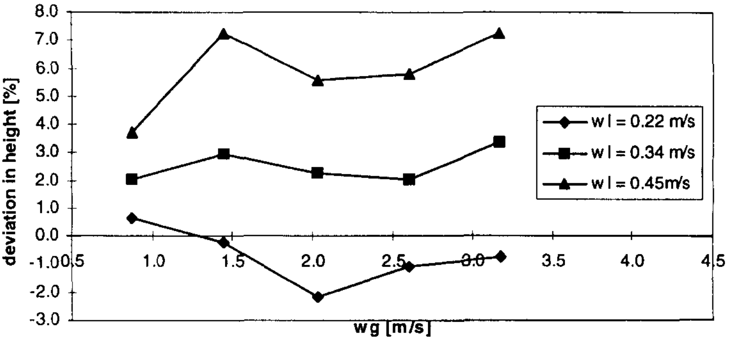

FIGURE 6. Height of the film absorber in comparison with the mass transfer model

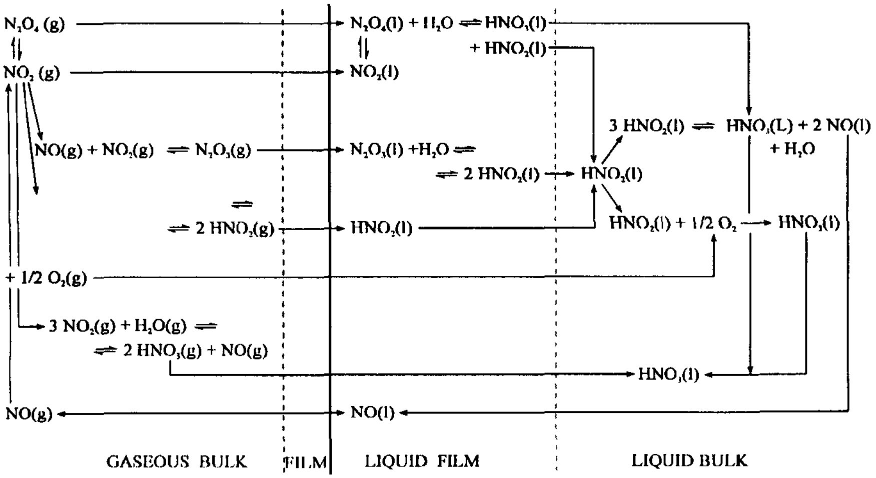
$N_2O_4$ (g)
$NO_2$ (g)
$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$
$\rightleftharpoons 2\ HNO_2(g)$
$+ 1/2\ O_2(g)$
$3\ NO_2(g) + H_2O(g) \rightleftharpoons$
$\rightleftharpoons 2\ HNO_3(g) + NO(g)$
NO(g)
$N_2O_4(l) + H_2O \rightleftharpoons HNO_3(l)$
$+ HNO_2(l)$
$NO_2(l)$
$N_2O_3(l) + H_2O \rightleftharpoons$
$\rightleftharpoons 2\ HNO_2(l)$
$HNO_2(l)$
NO(l)
$3\ HNO_2(l) \rightleftharpoons HNO_3(L) + 2\ NO(l)$
$+ H_2O$
$HNO_2(l)$
$HNO_2(l) + 1/2\ O_2 \rightarrow HNO_3(l)$
$HNO_3(l)$
GASEOUS BULK
FILM
LIQUID FILM
LIQUID BULK

FIGURE 7. Absorption mechanism of $NO_x$ in water (24)

## Test of Urea

$$CO(NH_2)_2 + 2\,HNO_2 \Rightarrow 2\,N_2 + CO_2 + 3\,H_2O \qquad (31)$$

Urea, which has successfully been applied in selective catalytic reduction of $NO_x$, is also known for its ability to reduce aqueous $HNO_2$ to nitrogen and water under strongly acidified conditions (25, 29). Its application led to the result that the activity does not differ from the absorption properties of pure water. In accordance with the products formed during absorption of $NO_2$ in water, increasing concentrations of nitrate in the aqueous phase were observed.

## Test of the Redox-system Cr(II)/Cr(III)

$$Cr^{3+} + e^- \Leftrightarrow Cr^{2+} \qquad E_0 = -0.41\ V \qquad (32)$$

Compared to urea and oxalic acid the redox-system Cr(II)/Cr(III) is a reversible redox-system. Practical tests showed, that this additive is not able to remove NO by redox-absorption. $NO_2$ is well absorbed, but it is definitely converted to $N_2O$ only and therefore not permitted for the absorption of $NO_x$.

## Test of the Redox-system Sulfite/Sulfate

$$SO_4^{2-} + H_2O + 2\,e^- \Leftrightarrow SO_3^{2-} + 2\,OH^- \qquad E_0 = -0.90\ V \qquad (33)$$

Literature reports successful absorption of NO when absorption takes place simultaneously with $SO_2$. $SO_2$ is oxidized by forming sulfuric acid, while NO is reduced. The additional use of the carrier Fe(II) is necessary, as $SO_2$-carriers (e.g., $Na_2SO_3$) themselves do not show sufficient reactivity (26 ,27). This process does not leave gaseous products only. Several aqueous by-products are formed too.

In general NO cannot be removed from off-gas by absorption without previous oxidation to $NO_2$ except, when using the additive Fe-II, which is able to form a nitrosyl complex. The second process, which is able to remove NO without pretreatment, the coabsorption process with $SO_2$ causes the formation of liquid byproducts. Technical applicability of these processes is therefore limited too.

Test of the Redox-system $NO_x$/Diamide

With regard to the electrochemical potential, diamide should enable promising separation results. The further investigations have therefore been concentrated on the activity of this additive.

As mentioned and as reported in literature (11), $NO_2$-absorption depends very much on the initial $NO_2$-content of the gaseous phase. The main reason is the instant formation of $N_2O_4$ from $NO_2$. The Henry coefficient of $N_2O_4$ is smaller than the Henry coefficient of $NO_2$ (table 1). Therefore the amount of $NO_x$-absorption in pure water decreases with decreasing $NO_2$-content in the feed gas, as demonstrated by figure 8.

As shown by figure 8, the amount of absorption of $NO_2$ in water covers a wide range of absorptivity and it depends on the feed content of $NO_2$. Increasing the content of the additive diamide causes an increase of absorption too. It finally leads to a complete removal of $NO_2$ at elevated concentration of diamide, independent of the initial $NO_2$-content. At a diamide concentration of 1 M the conditions for a gas-phase controlled mass transfer process should therefore be achieved. Increasing the temperature will enable the same result at lower concentration of diamide in the aqueous phase, as demonstrated by figure 9.

In a further step NO/$NO_2$-mixtures have been absorbed in dilute aqueous diamide at 293 K. The mixture of the nitrous gas has been varied from 0 - 100 % and the total $NO_x$-content between 10 and 1000 ppmv. Figure 10 shows the ratio of absorption with a feed content of 10 ppmv $NO_x$. As shown, $NO_2$ is completely absorbed (according to its feed, coabsorption of NO is indicated by the total ratio of absorption). $N_2O$-formation was not detected.

In a further step the experiment was repeated with an increased feed content of 100 ppmv $NO_x$ (NO + $NO_2$) as demonstrated by figure 11. The experiment resulted in similar absorption behavior. Coabsorption of NO caused the formation of $N_2O$. The maximum formation of $N_2O$ was detected at a ratio of NO/$NO_2$ of 1 and seems to be symetric to the NO/$NO_x$ ratio.

Coabsorption of NO and formation of $N_2O$ increases with increasing feed content. As shown by figure 12 the formation of $N_2O$ passes a maximum at a ratio of NO/$NO_2$ of 1 in general. According to figure 10-12 the reduction of NO is of the same amount as the formation of $N_2O$. Comparing the formation of $N_2O_3$ in the gaseous phase with the

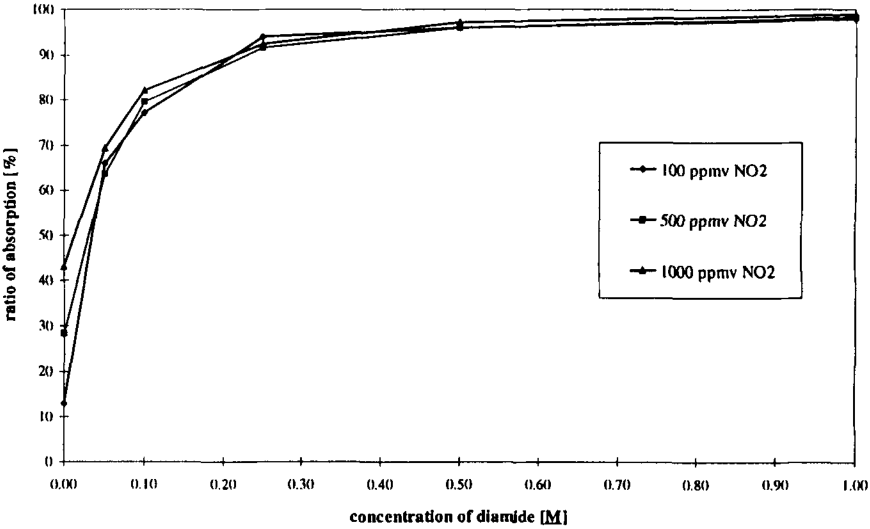

FIGURE 8. Absorption of $NO_2$ in aqueous solution of diamide at 293 K and ambient pressure. The initial $NO_2$-content and the concentration of diamide have been varied.

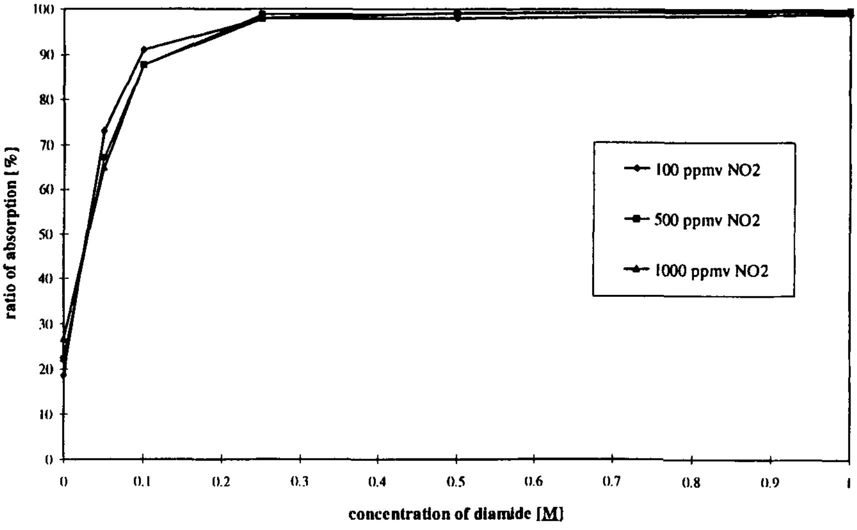

FIGURE 9. Absorption of $NO_2$ in aqueous solution of diamide at 313 K and ambient pressure. The initial $NO_2$-content and the concentration of diamide have been varied.

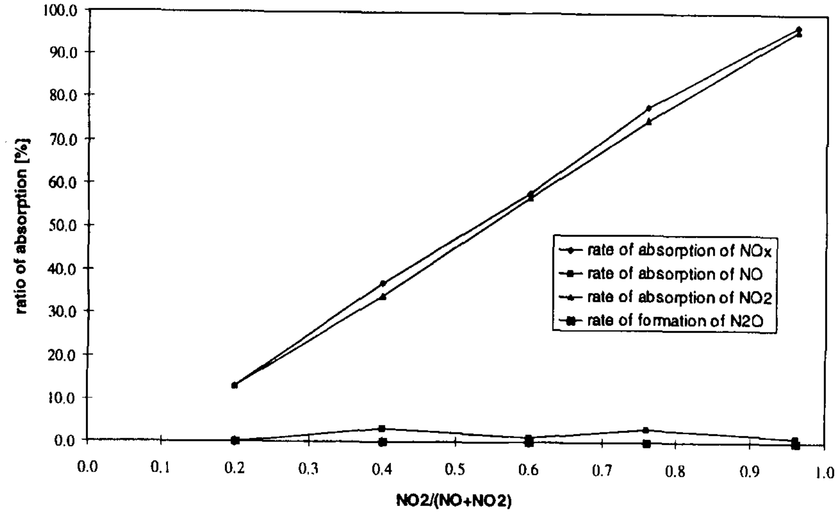

FIGURE 10. Rate of $NO_x$-absorption; feed gas: 10 ppmv $NO_x$; T=293 K; diamide: 1 M

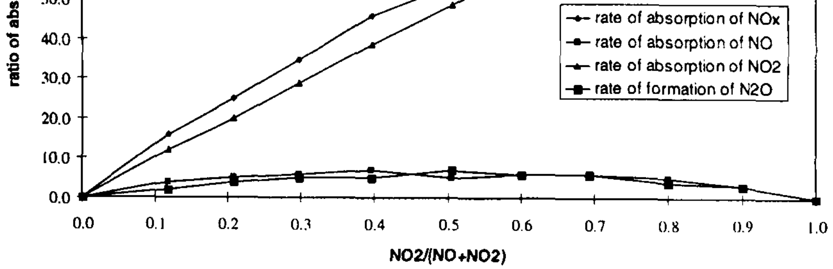

FIGURE 11. Rate of $NO_x$-absorption; feed gas: 100 ppmv $NO_x$; T=293 K; diamide: 1 M

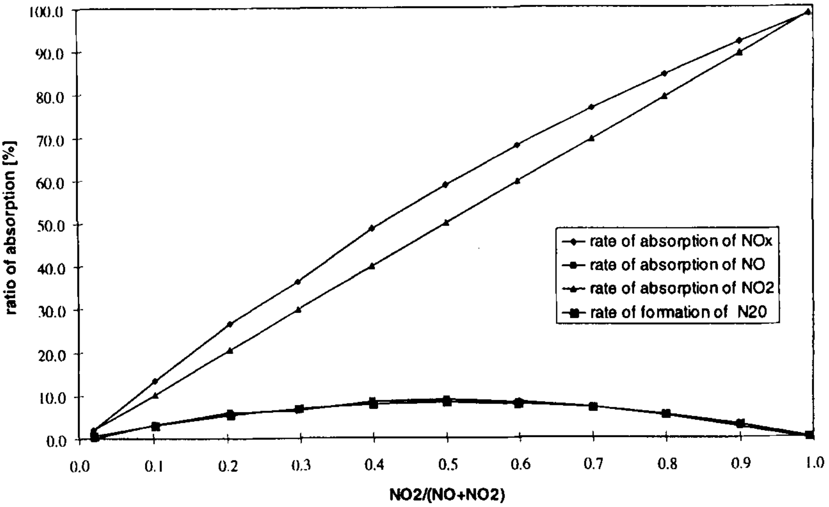

FIGURE 12. NO$_x$-absorption rate, 500 ppmv NO$_x$ in the feed gas, T=293 K, 1 M diamide

formation of $N_2O$ in the impinger shows similar results (see equations 3,8 and figure 2). This indicates the mechanism of reaction:

$$NO\,(g) + NO_2\,(g) \Leftrightarrow N_2O_3\,(g) \qquad (3)$$

$$N_2O_3 + N_2H_4 \Leftrightarrow N_2O + N_2 + 2H_2O \qquad (34)$$

Figure 13 shows the results of the investigation of the effect of temperature on the formation of $N_2O$.

With regard to technical application, which demands absorptive denoxing processes without byproducts (e.q. $N_2O$), NO has to be completly oxidized in a first step and can then be absorbed quantitatively in dilute aqueous diamide.

During the second part of the program mass transfer of $NO_2$-absorption was investigated.

Compared with the theoretical value of gase-phase controlled absorption, has been derived from equation 20-28, the absorption of $NO_2$ by dilute aqueous diamide is also affected by the reaction in the liquid phase. Figure 14 demonstrates the comparison of the mass transfer of $NO_2$ when using the solvents water and dilute aqueous diamide.

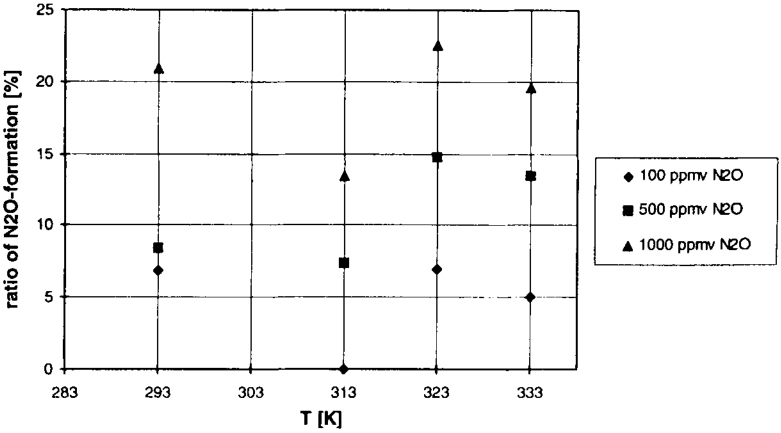

FIGURE 13. $N_2O$-formation; temperature: 293 - 333 K; ratio of $NO/NO_2=1$

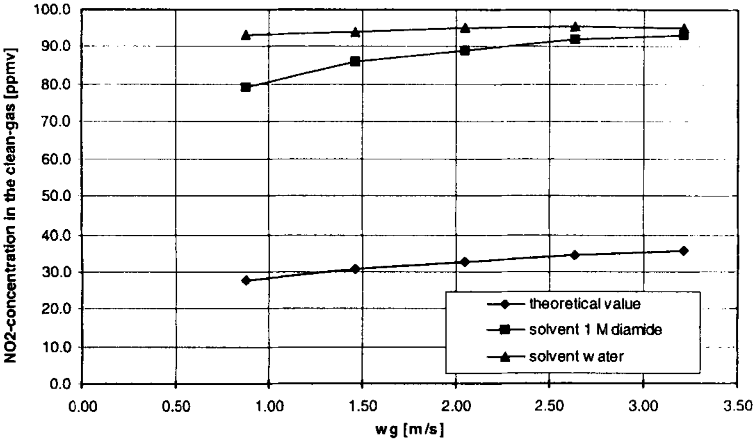

FIGURE 14. Investigation of the mass transfer of $NO_2$ at ambient temperature and pressure; gaseous feed content: 100 ppmv $NO_2$ ; diamide: 1 M

As reported in the literature (11), $NO_2$-absorption in water depends very much on the concentration of $NO_2$ in the feed gas. The reason is based on the instant equilibrium of $NO_2$ with the dimer $N_2O_4$ (figure 2). Absorptivity passes a minimum at a feed content of 100 ppmv, as shown by figure 15. This minimum is caused by the intersection of two different mechanismn of absorption. When considering smaller feed contents, the absorptivity is controlled by the reaction of $NO_2$ with the solvent. With increasing feed contents the mass transfer is affected by the instant formation of $N_2O_4$ in the gas-phase. As shown by table 1, the Henry coefficient of $N_2O_4$ is smaller compared with the Henry coefficient of $NO_2$. Mass transfer, determined by $N_20_4$ absorption, must therefore increase with increasing $NO_2$-content.

## SUMMARY

The chemical fundamentals and the basic mass transfer problems of several absorption processes have been investigated. The objective of the program has been the evaluation of processes for the separation of nitrogen monoxide. The investigations have been based on the redox-reaction

$$2\,NO + 4\,H^+ + 4\,e^- \Rightarrow N_2 + 2\,H_2O.$$

Within this program several additives in aqueous solutions (e.q. acidified hydroquinone, oxalic acid, diamide, urea, Cr(II)/Cr(III), sulfanilic acid, sodium sulfite and acidified iron sulfate + simultaneous absorption of $SO_2$) have been investigated.

Investigation has led into two directions. On one hand, the mechanism of absorption and the formation of products have been investigated. On the other hand mass transfer data have been evaluated. Before carrying out the experiments, the equipment was calibrated with the test system $SO_2$/air/solvent. A model, considering gas phase controlled mass transfer was applied.

NO-absorption only occured with acidified iron sulfate in presence of $SO_2$ which causes the formation of liquid by-products. Technical applicability of this process is therefore very limited. These investigations have led to the result that, in general, NO cannot be removed from off-gas by absorption without prior oxidation to $NO_2$.

Beside several additives of interest the program has centered on the investigation of the absorption properties of dilute aqueous diamide. Diamide use leads to a complete removal

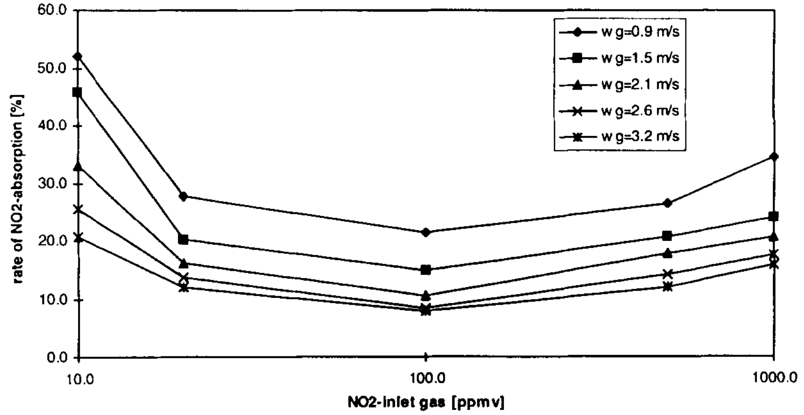

FIGURE 15. Mass transfer experiments dependent upon $NO_2$ feed concentration in 1 M diamide solutions at ambient temperature and pressure

of $NO_2$. Increasing the temperature will enable a similar result at lower concentration of diamide in the aqueous phase.

In a further step $NO/NO_2$-mixtures have been absorbed in dilute aqueous diamide. Co-absorption of NO and formation of $N_2O$ increases with increasing total feed content. The formation of $N_2O$ passes a maximum at a ratio of $NO/NO_2$ of 1 in general. Comparing the formation of $N_2O_3$ in the gaseous phase with the formation of $N_2O$ in the impinger shows similar results. This indicates the reaction mechanism

$N_2O_3 + N_2H_4 \Leftrightarrow N_2O + N_2 + H_2O$.

Compared with the theoretical value of gaseous mass transfer controlled absorption, which has been derived from the evaluated mass transfer model from the literature, the absorption of $NO_2$ by dilute aqueous diamide is also affected by the reaction in the liquid phase at small feed contents. When increasing the feed content, absorption is positively affected by $N_2O_4$, which is instantaneously formed from $NO_2$.

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