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# Removal of Nitrogen Dioxide and Sulfur Dioxide from Air Streams by Absorption in Urea Solution

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## ABSTRACT

*The study focuses on the absorption rates of $NO_2$, $SO_2$ and a mixture of these two acid gases into urea solution in packed bed column. The absorption rate was studied as a function of absorbent temperature, urea concentration and acid gas concentration. The influence of liquid temperature between 10 - 40˚C, urea concentration between 0.1 - 0.5 M and acid gas concentration $NO_2$ between 100 - 1000 ppm (191 - 1910 mg/m³), $SO_2$ between 500 - 2500 ppm (1310 - 6530 mg/m³) were investigated. The mass gas flow rate of 20.646 (kg/m².min) at 25˚C and the absorption rate were determined by measuring the $NO_2$ and $SO_2$ concentrations in the inlet and outlet streams of the absorptioncolumn. The absorption rate of $SO_2$ increases with the decrease of temperature of absorbent (urea solution) and with the increase of the urea concentration. The presence of $NO_2$ in the effluent gas stream lowers the absorption rate of $SO_2$ in urea solution due to the fast reaction of $NO_2$ with urea as compared with $SO_2$. The absorption rate of $NO_2$ decreases as the urea concentration exceeds 0.4 mol/l and for $NO_2$ gas concentration of 100 ppm due to the decrease the diffusivity of the gas. The experimental data were analyzed using dimensionless analysis to find the correlation of mass transfer coefficient in the packed column $Sh \, (H/dp)^{1.2} = 4.19 \times 10^{-2} \times (G' \, dp/\mu_g)^{0.87} (\mu_g/\rho_g \, D_{AB})^{0.60}$ The results confirmed the hypothesis that the absorption is accompanied with chemical reaction. Also it is found the increasing the temperature of absorbent solution the absorption rate of two gases is decreases. The mass transfer coefficient models are in good agreements with the Kramer's equation.*

## 1. Introduction

The harmful effects of the sulfur dioxide, $SO_x$ and nitrogen dioxide, $NO_x$, gases emissions in dense industrial and urban areas receive increasing attention especially where their production exceeds neutralization and dispersion forces [1]. Of the major contributors nitric acid plants contribute the most $NO_2$ to the environment [2]. The release of $SO_x$ can be controlled by ammonia injection which relies solely on gas phase reaction in the presence of moisture to produce ammonium sulfate solid particles that can be captured by any other particulate collection device [3]. Heterogeneous reduction process of $SO_x$ by hydrogen sulfide into sulfur can be done in the presence of suitable solid phase catalysts. Methane can be used for the reduction of $SO_x$ into hydrogen sulfide on alumina as the catalyst. The hydrogen sulfide produced by this method is captured by amine scrubbing of the reduced gas stream. The higher concentration of sulfide obtained

by heating the amine salt may then be easily and economically converted to elemental sulfur via the Claus process [4].

Catalytic oxidation of $SO_x$ with air, via the heterogeneous contact process or the homogeneous chamber process, also serves to improve the collection efficiency of the $SO_2$. Also the collection of $SO_3$ by direct absorption into water is extremely efficient and the produced sulfuric acid is a salable commodity [5]. The scrubbing of $SO_2$ in dilute ammonium hydroxide gives ammonium sulfate that can be a valuable constituent of fertilizer formulations [6]. The Wellman-lord process uses the effective sodium sulfite equilibrium to capture sulfur dioxide from flue gases [7]. Most of the sodium bisulfite produced is converted back to sodium sulfite which can be crystallized out, dried and sold as wood pulping chemical. The citrate process in which much development work has been invested by the U.S Bureau of mines and by Pfizer use an aqueous solution of citric acid to

capture $SO_2$. Uncomplexed citric acid can be regenerated thermally to obtain stripped citrate solution and stream of up to 90% $SO_2$ at this stage [8].

The $SO_2$ gas may be entrapped in molten alkali carbonate at about 425°C [9]. Limestone or lime slurry in water is used in a suitably designed scrubber in an effective and relatively low cost $SO_2$ removal method. The affinity of the activated carbon for the acid gases is, in increasing order, $CO_2 < SO_2 < NO_2$, [10]. The use of powdered limestone injection is applied to remove $SO_2$ from flue gases from coal burning. The $SO_2$ reacts with solid lime to form solid particles of calcium sulfite and calcium sulfate which are captured in electrostatic precipitators [11].

Three methods are used to control and reduce $NO_x$ emission, namely: absorption, selective catalytic reduction and non-sélective catalytic reduction [12]. For methane reduction, the polluted gas stream is preheated to about 400°C and then blended with the appropriate proportion of methane before passage over platinum or palladium catalytic surface for reduction [13]. Selective catalytic abatement uses a catalyst and ammonia fuel to reduce $NO_x$ in preference to combustion with the much higher levels of oxygen in the gas at temperatures in the range 210 - 410°C. Slight excess of ammonia may be used to leave 5 - 20 (ppmv) in the treated gas stream. Zhang *et al.*, 2008 [14], studied the $NO_x$ removal from simulated flue gas by chemical absorption-biological reduction integrated approach in a biofilter. They concluded that maximum elimination capacity (18.78 g·NO $m^{-3}$ $h^{-1}$) was achieved at a loading rate of 28.68 g·NO $m^{-3}$ $h^{-1}$ and maintained 5 h operation at the steady state.

The aim of the present work is at studying the effects of the operation parameters on the absorption of $SO_2$ and $NO_2$ from air streams using dilute urea solution. The operating variables studied are: concentration of the two gases in air, concentration of absorbent (urea) solution and temperature of absorbent solution

## 2. Materials and Methods

### 2.1. Experimental Set up

**Figure 1** shows a photograph of the bench scale system designed for the absorption of gases. The rig consisted of three sections: generation, absorption and analysis sections.

For the generation of the gases a three neck QVF 5 L-flask is connected at its upper part to a glass burette (100 ml) capacity which contains sulfuric acid or nitric acid. The inlet of the generation section was connected to a compressed air source.

The absorption section was a packed column of 7.5 cm inside diameter and 50 cm height, which is packed with glass Rashig rings (6 mm inside diameter). The height of packing is (45 cm). Counter current flow of the gas mixture was maintained at a mass flux of gases (G' = 20.64 kg/m²·min), and the mass flux of absorbent liquid downward = 188 kg/m²·min. The used values for the gas flow rate and liquid flow rate was checked with loading, flooding and pressure drop calculation in the column. Calculations are given in appendix C. The pump is used to rises the absorbent solution from the 15 liter capacity (QVF) vessel supported at the middle of column. The rig was insulated with glass wool to maintain the absorbent temperature nearly constant.

Calibrated rotameters were used to measure the air and solvent flow rates.

### 2.2. Chemicals

For the generation and detection of $SO_2$, Sodium sulfite, $Na_2SO_3$ was supplied from Merck, Germany. Sulfuric acid, $H_2SO_4$, iodine, $I_2$, Iodine ampoule, 0.1 N, potassium iodide, KI, starch and Sodium thiosulfate ampoule, 0.1 N were analytical grade reagents from BDH, England. Urea was an industrial grade product from a local fertilizer factory.

For the generation and detection of $NO_2$, nitric acid, sodium hydroxide, phenolphthalein and copper were supplied from BDH, England; Hydrogen peroxide, $H_2O_2$ was a local product.



**Figure 1. A photograph of the experimental Rig.**

## 2.3. Procedures

$SO_2$ Generation was carried out by the reaction of sodium sulfite solution with sulfuric acid using various acid concentrations (5 - 23 wt%). An air stream at constant mass flux of (20.64 kg/m$^2$·min) was then passed through the reaction vessel to transport the generated $SO_2$ gas towards the packed bed absorber. Urea solution was allowed to move downward from the top of the column at constant mass flux (188 kg/m$^2$·min).

NO$_2$ was generated by the reaction of copper with nitric acid of various concentrations (5 - 35 wt%). An air stream at constant mass flux of (20.64 kg/m$^2$·min) was then passed through the reaction vessel to transport the generated $NO_2$ gas towards the packed bed absorber. Urea solution was allowed to move downward from the top of the column at constant mass flux (188 kg/m$^2$·min).

Generation of $SO_2$ and $NO_2$ mixture:

Two reaction vessels were used simultaneously to generate the two gases as in the procedure above and the gases were directed at the same time by the same air stream towards the absorption column. The outlet of the column was connected to two different traps containing the detection reagents of residual gases sequentially, where the first absorber trap contains iodine solution for $SO_2$ and the second contains hydrogen peroxide for $NO_2$.

## 2.4. Measurements of Absorption Rate

The weight of $SO_2$ Absorbed was determined by measuring the residual amount by its quantitative reaction with iodine and titrating excess iodine with sodium thiosulfate. The number of iodine equivalents is equal to the residual $SO_2$ in the trap.

**The weight of $NO_2$ absorbed by the quantitative reaction with** hydrogen peroxide to form nitric acid which can be determined by titration with 0.01 N NaOH solution using phenolphthalein as an indicator [15].

## 2.5. Experimental Design

Variables acting together may have greater or smaller effect than individual variables acting alone. A response surface can be most efficient fitted if proper attention is given to the choice of experimental design [16]. Box-Wilson, composite rotatable design is common type of statistical experiments, especially applicable to optimization analysis.

The effect of three variables for each acid gas such as, liquid temperature, liquid concentration and concentration of $SO_2$ and $NO_2$ on the absorption rates were investigated and analyzed. The number of experiments needed according to design are 15 plus 5 experiments at the center point to estimate the experimental error.

For $SO_2$ gas, the ranges of the operating variables are:

1) $SO_2$ concentration, 500 - 2500 ppm (1310 - 6550 mg/m$^3$) = $X_1$
2) Urea concentration, 0.1 - 0.5 mol/L = $X_2$
3) Liquid temperature, 10 to 40°C = $X_3$

According to Equation (1) the relationships between the coded levels and the corresponding real variables as follows

$$X_{1coded} = \frac{conc.SO_2 - 1500}{577.35} \qquad (10)$$

$$X_{2coded} = \frac{Urea.conc(mol/l) - 0.3}{0.1154} \qquad (11)$$

$$X_{3coded} = \frac{Tempofsolution(°C) - 25}{8.66} \qquad (12)$$

For $NO_2$ gas, the ranges of the operating variables are:
1) $NO_2$ concentration, 100 - 1000 ppm (191 - 1910 mg/m$^3$) = $X_1$
2) Urea concentration, 0.1 - 0.5 mol/L = $X_2$
3) Liquid temperature, 10 to 40°C = $X_3$

According to Equation (1) the relationships between the coded levels and the corresponding real variables are as follows

$$X_{1Coded} = \frac{Conc.NO_2 - 550}{260} \qquad (13)$$

$$X_{2coded} = \frac{Conc.urea - 0.3}{0.1154} \qquad (14)$$

$$X_{3Coded} = \frac{Temp(°C) - 25}{8.66} \qquad (15)$$

## 2.6. For $SO_2$ and $NO_2$ Gases

1) $SO_2$ concentration, 500 - 2500 ppm (1310 - 6550 mg/m$^3$) = $X_1$
2) $NO_2$ concentration, 100 - 1000 ppm (191 - 1910 mg/m$^3$) = $X_2$
3) Urea concentration, 0.1 - 0.5 mol/L = $X_3$
4) Liquid temperature, 10 to 40°C = $X_4$

$$X_{1coded} = \frac{Conc.SO_2 - 1500}{500} \qquad (16)$$

$$X_{2coded} = \frac{Conc.NO_2 - 550}{225} \qquad (17)$$

$$X_{3coded} = \frac{Conc.urea - 0.3}{0.1} \qquad (18)$$

$$X_{4coded} = \frac{Temp(°C) - 25}{7.5} \qquad (19)$$

The values of the coded and real variables for the absorption experiments of $SO_2$/$NO_2$ mixtures are given in **Table 1**.

**Table 1. Coded and real variables for $SO_2$ and $NO_2$ absorption experiments.**

| Run no. | Coded Variables | | Real Variables | | | |
|---|---|---|---|---|---|---|
| | $X_1/X_2/X_3X_4$ | $ConSO_2$ (ppm) | $ConcNO_2$ (ppm) | Urea. Conc. (gmol/l) | Temp of Absorbent $^0C$ |
| 1 | +1/+1/+1/+1 | 2000 | 775 | 0.4 | 32.5 |
| 2 | −1/+1/+1/+1 | 1000 | 775 | 0.4 | 32.5 |
| 3 | +1/−1/+1/+1 | 2000 | 225 | 0.4 | 32.5 |
| 4 | +1/+1/−1/+1 | 2000 | 775 | 0.2 | 32.5 |
| 5 | +1/+1/+1/−1 | 2000 | 775 | 0.4 | 17.5 |
| 6 | −1/−1/−1/−1 | 1000 | 225 | 0.2 | 17.5 |
| 7 | +1/−1/−1/−1 | 2000 | 225 | 0.2 | 17.5 |
| 8 | −1/+1/−1/−1 | 1000 | 775 | 0.2 | 17.5 |
| 9 | −1/−1/+1/−1 | 1000 | 225 | 0.4 | 17.5 |
| 10 | −1/−1/−1/+1 | 1000 | 225 | 0.2 | 32.5 |
| 11 | +1/+1/−1/−1 | 2000 | 775 | 0.2 | 17.5 |
| 12 | +1/−1/+1/−1 | 2000 | 225 | 0.4 | 17.5 |
| 13 | +1/−1/−1/+1 | 2000 | 225 | 0.2 | 32.5 |
| 14 | −1/−1/+1/+1 | 1000 | 225 | 0.4 | 32.5 |
| 15 | −1/1/−1/1 | 1000 | 775 | 0.2 | 32.5 |
| 16 | −1/1/1/−1 | 1000 | 775 | 0.4 | 17.5 |
| 17 | 2/0/0/0 | 2500 | 550 | 0.3 | 25 |
| 18 | 0/2/0/0 | 1500 | 1000 | 0.3 | 25 |
| 19 | 0/0/2/0 | 1500 | 550 | 0.5 | 25 |
| 20 | 0/0/0/2 | 1500 | 550 | 0.3 | 40 |
| 21 | −2/0/0/0 | 500 | 550 | 0.3 | 25 |
| 22 | 0/−2/0/0 | 1500 | 100 | 0.3 | 25 |
| 23 | 0/0/−2/0 | 1500 | 550 | 0.1 | 25 |
| 24 | 0/0/0/−2 | 1500 | 550 | 0.3 | 10 |
| 25 | 0/0/0/0 | 1500 | 550 | 0.3 | 25 |
| 26 | 0/0/0/0 | 1500 | 550 | 0.3 | 25 |
| 27 | 0/0/0/0 | 1500 | 550 | 0.3 | 25 |
| 28 | 0/0/0/0 | 1500 | 550 | 0.3 | 25 |
| 29 | 0/0/0/0 | 1500 | 550 | 0.3 | 25 |

# 3. Results and Discussion

The measurement concerned the study of the effect of the operation variables such as $SO_2$ and $NO_2$ level, urea concentration and operating temperature on the absorption rate of acid gas and consequently their removal.

The absorption rate of an acid gas ($NO_2$ or $SO_2$) is expressed as the equivalent moles of $NO_2$ or $SO_2$ that react with urea solution per unit interface area per unit time. This absorption rates were calculated in accordance with the expressions of Weisweiler and Dieb [17]. The absorption rates values for $SO_2$ and $NO_2$ are listed in the **Tables 2** and **3**, respectively. The mass transfer coefficient for the packed bed column was estimated by using the design equation for dilute gas mixture [18].

## 3.1. Effect of Operating Variables

### 3.1.1. Effect of Acid Gas Concentration
**Figure 2** shows the effect of $SO_2$ concentrations on the absorption rate for various urea concentrations (0.1 - 0.5 mol/L at fixed absorbent solution temperature of 25˚C. For $NO_2$ the results are shown in **Figure 3**. The results indicate that the absorption rate increases as the $SO_2$

concentration increases. This can be attributed to the greater driving force available as the $SO_2$ concentration increased and consequently higher absorption rate are more easily attained. These results agree with published report of Basu *et al.* [19], where the rate of absorption increased directly with the driving force during the $SO_2$ absorption in caustic soda and dimethylaniline solution.

The results of $NO_2$ indicated that the absorption rate increases sharply as the concentration of the gas increases. This behavior may be expected because the reaction between $NO_2$ and urea solutions in the liquid phase is very fast. These results confirm the findings of Lefer *et al.* [20].

**Figure 4** shows the effect of $NO_2$ concentrations on the absorption rate for various working temperatures (10 - 40˚C) at fixed urea concentration of 0.185 M. For $SO_2$ the results indicated a similar trend. The absorption rate increases as the $SO_2$ and $NO_2$ concentrations in- creased. Also, these figures indicate that the absorption rate is more favored at lower temperatures. Thus the re- action rate is higher at lower temperatures because the diffusivity increasing with decreasing temperature.

**Table 2. Experimental results of SO$_2$ absorption and values of interfacial area of packing.**

| Run No. | SO$_2$ input Conc., ppm | SO$_2$ Output Conc., ppm | $a_p$ (m$^2$/m$^3$) | a(m$^2$) | Na *10$^{-3}$ (mol/m$^2$.s) | $K_G$ (kg/m$^3$ s (kN/m$^2$) |
|---|---|---|---|---|---|---|
| 1 | 922.6 | 156.842 | 175.3678 | 0.073 214 | 0.476 972 | 0.000 168 352 |
| 2 | 2077.6 | 276.3208 | 175.3678 | 0.073 214 | 1.121 972 | 0.000 191 671 |
| 3 | 922.6 | 52.957 24 | 175.4981 | 0.073 268 | 0.541 277 | 0.000 271 306 |
| 4 | 2077.6 | 49.654 64 | 175.4981 | 0.073 268 | 1.262 219 | 0.000 354 488 |
| 5 | 922.6 | 204.7618 | 183.8415 | 0.076 752 | 0.426 515 | 0.000 136 429 |
| 6 | 2077.6 | 386.2051 | 183.8415 | 0.076 752 | 1.004 968 | 0.000 152 494 |
| 7 | 922.6 | 107.0216 | 183.9731 | 0.076 807 | 0.484 242 | 0.000 195 092 |
| 8 | 2077.6 | 120.5008 | 183.9731 | 0.076 807 | 1.162 009 | 0.000 257 866 |
| 9 | 500 | 130 | 180.1686 | 0.075 218 | 0.224 323 | 0.000 124 574 |
| 10 | 2500 | 162.5 | 180.1686 | 0.075 218 | 1.417 175 | 0.000 252 774 |
| 11 | 1500 | 170.835 | 180.0638 | 0.075 174 | 0.806 313 | 0.000 201 026 |
| 12 | 1500 | 58.695 | 180.3642 | 0.075 3 | 0.872 884 | 0.000 299 381 |
| 13 | 1500 | 17.952 | 171.2891 | 0.071 511 | 0.945 113 | 0.000 430 476 |
| 14 | 1500 | 280.245 | 184.3118 | 0.076 948 | 0.722 887 | 0.000 151 648 |
| 15 | 1500 | 111 | 180.1686 | 0.075 218 | 0.842 12 | 0.000 240 782 |
| 16 | 1500 | 111 | 180.1686 | 0.075 218 | 0.842 12 | 0.000 240 782 |
| 17 | 1500 | 111 | 180.1686 | 0.075 218 | 0.842 12 | 0.000 240 782 |
| 18 | 1500 | 111 | 180.1686 | 0.075 218 | 0.842 12 | 0.000 240 782 |
| 19 | 1500 | 111 | 180.1686 | 0.075 218 | 0.842 12 | 0.000 240 782 |
| 20 | 1500 | 111 | 180.1686 | 0.075 218 | 0.842 12 | 0.000 240 782 |

**Table 3. Experimental results of NO$_2$ absorption and values of interfacial area of packing.**

| Run No. | NO$_2$ input Conc., ppm | NO$_2$ Output Conc., ppm | $a_p$ (m$^2$/m$^3$) | a(m$^2$) | Na*10$^{-3}$ (mol/m$^2$s) | $K_G$(kg/m$^3$s( kN/m$^2$) |
|---|---|---|---|---|---|---|
| 1 | 290 | 55.564 | 175.3678 | 0.073 214 | 0.148 201 | 0.000 113 |
| 2 | 810 | 125.631 | 175.3678 | 0.073 214 | 0.432 63 | 0.000 127 |
| 3 | 290 | 14.21 | 175.4981 | 0.073 268 | 0.174 214 | 0.000 206 |
| 4 | 810 | 21.06 | 175.4981 | 0.073 268 | 0.498 366 | 0.000 249 |
| 5 | 290 | 73.5266 | 183.8415 | 0.076 752 | 0.130 538 | 8.93E-05 |
| 6 | 810 | 176.5719 | 183.8415 | 0.076 752 | 0.381 971 | 9.92E-05 |
| 7 | 290 | 31.2098 | 183.9731 | 0.076 807 | 0.155 944 | 0.000 145 |
| 8 | 810 | 40.581 | 183.9731 | 0.076 807 | 0.463 645 | 0.000 195 |
| 9 | 100 | 20 | 180.1686 | 0.075 218 | 0.049 225 | 0.000 107 |
| 10 | 1000 | 39 | 180.1686 | 0.075 218 | 0.591 318 | 0.000 216 |
| 11 | 550 | 53.185 | 180.0638 | 0.075 174 | 0.305 876 | 0.000 155 |
| 12 | 550 | 28.7705 | 180.3642 | 0.0753 | 0.320 372 | 0.000 196 |
| 13 | 550 | 26.774 | 171.2891 | 0.071 511 | 0.338 638 | 0.000 211 |
| 14 | 550 | 102.7565 | 184.3118 | 0.076 948 | 0.269 009 | 0.000 109 |
| 15 | 550 | 23.65 | 180.1686 | 0.075 218 | 0.323 871 | 0.000 209 |
| 16 | 550 | 23.65 | 180.1686 | 0.075 218 | 0.323 871 | 0.000 209 |
| 17 | 550 | 23.65 | 180.1686 | 0.075 218 | 0.323 871 | 0.000 209 |
| 18 | 550 | 23.65 | 180.1686 | 0.075 218 | 0.323 871 | 0.000 209 |
| 19 | 550 | 23.65 | 180.1686 | 0.075 218 | 0.323 871 | 0.000 209 |
| 20 | 550 | 23.65 | 180.1686 | 0.075 218 | 0.323 871 | 0.000 209 |

### 3.1.2. Effect of Urea Concentration

**Figure 5** shows the effect of urea concentration on the absorption rate of $SO_2$ at various concentrations in the range (500 - 2500 ppm) and fixed absorbent temperature (25°C). It is clear that as the urea concentration increased, the absorption rate increases regularly. Also, a similar effect is obtained at various working temperature (10 - 40°C) and fixed $SO_2$ concentration (1500 ppm). When the urea concentration increased, the absorption rate increases, this agrees with the findings in the cases of using dimethylaniline as an absorbent as reported by Basu *et al.* [27]. The activity of urea solution towards the removal of sulfur dioxide may be due to the possible bonding of two $SO_2$ molecules to each urea molecule [21].

The results of $NO_2$ absorption at various concentrations (100 - 1000 ppm) and fixed absorbent temperature (25°C) showed a clear increase in the absorption rate as the urea solution increases. However, beyond 0.4 mol/l of urea, the absorption rate decreases especially at lower acid gas concentration. This trend may be attributed to the decrease the diffusivity of gas.
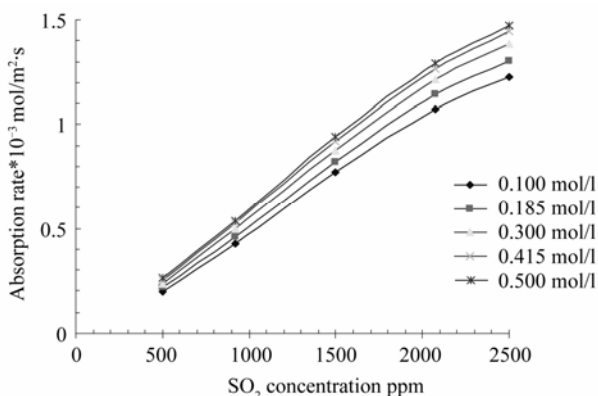
The effect of urea concentration on the absorption rate of $NO_2$ at different absorption temperature in the range (10 - 40°C) and constant nitrogen dioxide concentration (500 ppm) is shown in **Figure 6**. It is clear that as the urea concentration increased, the absorption rate increases. The activity of urea solution toward the removal of $NO_2$ may be due to fast bonding of $NO_2$ with urea molecules.

### 3.1.3. Effect of Temperature of Absorbent

The effect of the temperature of the absorbent on the absorption rate of $SO_2$ is shown in **Figure 7** at constant acid gas concentration and various urea concentrations in the range of (0.1 - 0.5) mol/l. The absorption rate is found to decrease considerably with increasing the temperature. At constant urea concentration and various $NO_2$ concentration in the range of $SO_2$ (500 - 2500) ppm and $NO_2$ (100 - 1000) ppm, the increase of absorbent temperature lowers the absorption rate of the two acid gases. Such a slightly decreasing rate at higher temperatures may be attributed to the decrease of the solubility and diffusivity of aid gases in urea solution as the temperature increased.
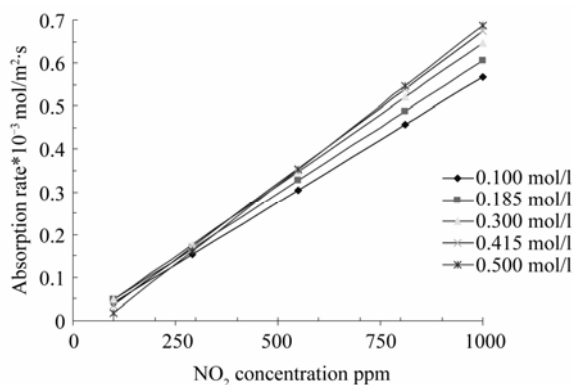


**Figure 2. Absorption rate as a function $SO_2$ concentration for various urea concentration.**



**Figure 3. Absorption rate as a function $NO_2$ concentration for different urea concentration.**
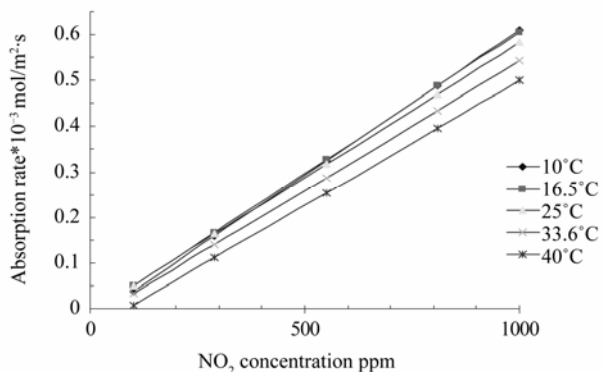


**Figure 4. Absorption rate as a function $NO_2$ concentration for different Temperatures of absorbent.**
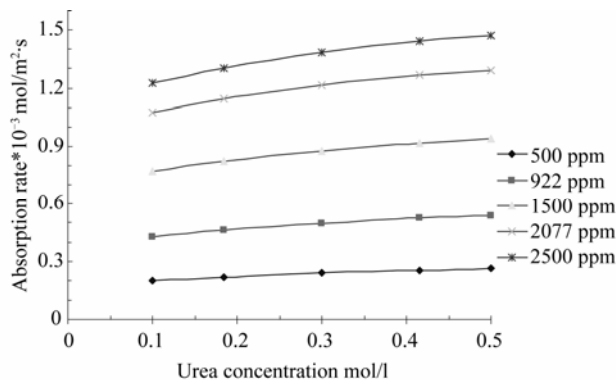


**Figure 5. Absorption rate as a function urea concentration for different SO2 concentration.**
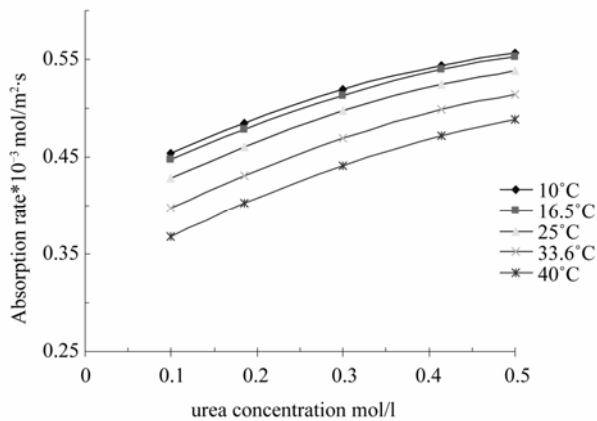
**Figure 6. Absorption rate of $NO_2$ as a function urea concentration for various temperatures.**



**Figure 7. Absorption rate of $SO_2$ as a function of temperature of absorbent for various urea concentrations.**

### 3.1.4. Effect of $NO_2$ on $SO_2$ Absorption Rate

**Figure 8** shows the absorption rate of $SO_2$ in the presence of various $NO_2$ concentrations at fixed temperature and urea concentration. There existed a minor decrease in the absorption rate decrease with the increase of $NO_2$ concentration. **Table 4** shows the experimental data and values of interfacial area of packing for $NO_2$ and $SO_2$. This slight decrease may be due to the fact that the rate of reaction of urea is faster with $NO_2$ than that with $SO_2$.

### 3.2. Mass Transfer Coefficient in Packed Tower

The majority of published results for mass transfer coefficients in packed towers are for rather small laboratory units of 50 - 250 mm diameter, and there is still some uncertainty in extending these data for use in industrial units. One of the great difficulties in correlating the performance of packed towers is the problem of assessing the effective wetted area for interface transfer. It is convenient to consider separately the conditions where the gas film controls the process, and then where the liquid film controls [18].

### 3.2.1. Postulating the Model

The mass transfer correlation is usually determined by using Buckingham method for dimensional analysis. The mass transfer coefficient is a function of more variable effect on this important parameter in packed bed column. The basic equation relating the variables is

$$K_G = f\left(dp\, D_{AB}\, G'\, \mu_g\, \rho_g\, H\right) \tag{20}$$

The variable and the dimensional constant believed to be involved and their dimensions in the engineering system are given below

$$\text{Mass transfer coefficient} = K_G = L/T \tag{21}$$
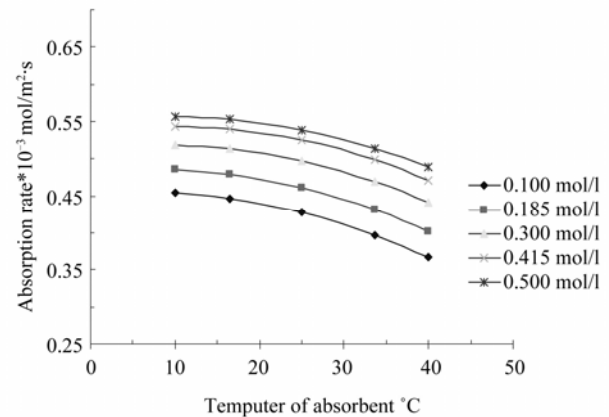
$$\text{Gas density} = \rho_g = (M/L) \tag{22}$$

$$\text{Gas viscosity} = \mu_g = (M/L.T) \tag{23}$$

$$\text{Diffusivity of gas} = D_{AB} = \left(L^2/T\right) \tag{24}$$

$$\text{Packing size} = dp = (L) \tag{25}$$

$$\text{Height of packing} = H = (L) \tag{26}$$

$$\text{Mass velocity of gas} \ G' = \left(M/T.L^2\right) \tag{27}$$

According to Buckingham theory

$$P = n - m = 7 - 3 = 4 \tag{28}$$

$P$ is equal to number of dimensionless group
Choosing the three virtual variable

$$dp = L \quad L = dp \tag{29}$$

$$D_{AB} = L^2/T \quad T = dp^2/D_{AB} \tag{30}$$

$$\rho_g = M/L^3 \quad M = \rho_g\, dp^3 \tag{31}$$

$$\prod_1 = \left(K_G\, dp/D_{AB}\right) \text{ this dimension is Sherwood number} \tag{32}$$
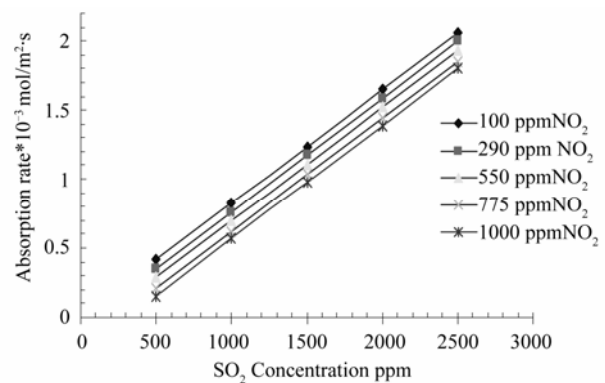


**Figure 8. Absorption rate as a function $SO_2$ concentration for various $NO_2$ concentrations.**

**Table 4. Experimental results of SO₂ and NO₂ absorption and values of interfacial area of packing.**

| Run | Inlet SO₂ ppm | Outlet SO₂ ppm | Inlet NO₂ ppm | Outlet NO₂ ppm | $a_p$ m²/m³ | $a_m$ m² | Na SO₂ mmol/m²·s | Na NO₂ mmol/m²·s | Kg (SO₂) m/s | Kg (NO₂) m/s |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2000 | 398.6 | 775 | 158.8 | 184.066 | 0.076 84 | 0.9503 | 0.3710 | 0.000 146 | 0.0001 |
| 2 | 1000 | 297.5 | 775 | 141.1 | 184.066 | 0.076 84 | 0.4168 | 0.3823 | 0.000 11 | 0.0001 |
| 3 | 2000 | 294 | 225 | 56.09 | 184.066 | 0.076 84 | 1.0124 | 0.1061 | 0.000 174 | 9.03E-5 |
| 4 | 2000 | 650.5 | 775 | 247.2 | 183.794 | 0.076 73 | 0.8020 | 0.3317 | 0.000 102 | 7.44E-05 |
| 5 | 2000 | 121.2 | 775 | 106.0 | 176.470 | 0.073 67 | 1.1629 | 0.4205 | 0.000 265 | 0.000 135 |
| 6 | 1000 | 262.5 | 225 | 57.84 | 176.352 | 0.073 62 | 0.4568 | 0.1050 | 0.000 126 | 9.22E-05 |
| 7 | 2000 | 321.2 | 225 | 80.28 | 176.352 | 0.073 62 | 1.0398 | 0.0910 | 0.000 173 | 6.99E-05 |
| 8 | 1000 | 327.5 | 775 | 148.8 | 176.470 | 0.073 67 | 0.4162 | 0.3774 | 0.000 105 | 0.000 112 |
| 9 | 1000 | 169 | 225 | 206.1 | 176.231 | 0.073 57 | 0.5150 | 0.0118 | 0.000 168 | 5.94E-06 |
| 10 | 1000 | 338.7 | 225 | 68.68 | 183.916 | 0.076 78 | 0.3927 | 0.0983 | 9.81E-05 | 7.72E-05 |
| 11 | 2000 | 461.2 | 775 | 222.2 | 176.470 | 0.073 67 | 0.9524 | 0.3328 | 0.000 139 | 8.47E-05 |
| 12 | 2000 | 60 | 225 | 39.78 | 176.231 | 0.073 57 | 1.2024 | 0.1117 | 0.000 332 | 0.000 118 |
| 13 | 2000 | 511.2 | 225 | 87.39 | 184.066 | 0.076 84 | 0.8835 | 0.0828 | 0.000 123 | 6.15E-05 |
| 14 | 1000 | 247.5 | 775 | 59.17 | 183.794 | 0.076 73 | 0.4472 | 0.1041 | 0.000 127 | 8.7E-05 |
| 15 | 1000 | 390 | 775 | 197.3 | 184.034 | 0.076 83 | 0.3620 | 0.3554 | 8.52E-05 | 8.9E-05 |
| 16 | 1000 | 200 | 775 | 41.23 | 176.427 | 0.073 65 | 0.4953 | 0.4510 | 0.000 152 | 0.000 199 |
| 17 | 2500 | 345 | 550 | 134.7 | 180.191 | 0.075 22 | 1.3063 | 0.2557 | 0.000 183 | 9.34E-05 |
| 18 | 1500 | 367.5 | 1000 | 194.2 | 180.364 | 0.075 3 | 0.6858 | 0.4761 | 0.000 13 | 0.000 109 |
| 19 | 1500 | 82.5 | 550 | 20.68 | 179.971 | 0.075 13 | 0.8603 | 0.3256 | 0.000 269 | 0.000 218 |
| 20 | 1500 | 407.5 | 550 | 145.9 | 187.602 | 0.078 32 | 0.6360 | 0.2487 | 0.000 116 | 8.46E-05 |
| 21 | 500 | 113.5 | 100 | 57.97 | 180.191 | 0.075 22 | 0.2342 | 0.3026 | 0.000 137 | 0.000 149 |
| 22 | 1500 | 156.6 | 550 | 17.79 | 180.063 | 0.075 17 | 0.8148 | 0.0530 | 0.000 209 | 0.000 115 |
| 23 | 1500 | 442.5 | 550 | 162.7 | 180.201 | 0.075 23 | 0.6410 | 0.2382 | 0.000 113 | 8.09E-05 |
| 24 | 1500 | 97.5 | 550 | 23.87 | 171.910 | 0.071 77 | 0.8911 | 0.3236 | 0.000 265 | 0.000 218 |
| 25 | 1500 | 265.5 | 550 | 85.47 | 180.191 | 0.075 22 | 0.7483 | 0.2857 | 0.000 16 | 0.000 124 |
| 26 | 1500 | 265.5 | 550 | 85.47 | 180.191 | 0.075 22 | 0.7483 | 0.2857 | 0.000 16 | 0.000 124 |
| 27 | 1500 | 265.5 | 550 | 85.47 | 180.191 | 0.075 22 | 0.7483 | 0.2857 | 0.000 16 | 0.000 124 |
| 28 | 1500 | 265.5 | 550 | 85.47 | 180.191 | 0.075 22 | 0.7483 | 0.2857 | 0.000 16 | 0.000 124 |
| 29 | 1500 | 265.5 | 550 | 85.47 | 180.191 | 0.075 22 | 0.7483 | 0.2857 | 0.000 16 | 0.000 124 |

$$\prod_2 = \left( \mu_g / \rho_g \, D_{AB} \right) \quad \text{this dimension is Schmidt number}$$

(33)

$$\prod_3 = \left( G' \, dp / \mu_g \right) \quad \text{this dimension is Reynolds number}$$

(34)

$$\prod_4 = \left( dp / H \right)$$

(35)

These four dimensionless groups are frequently used in mass transfer coefficient correlation. Functionally, their relation may be expressed as

$$\Phi \left( Sh, Re, Sc, \left( dp/H \right) \right) = 0$$

(36)

Or as $\quad Sh = \Phi_1 \left( Re, Sc, \left( dp/H \right) \right)$

(37)

It has been found that these dimensionless groups may be correlated well by equation of the type

$$\left( K_G \, dp / D_{AB} \right) = K \left( G' \, dp / \mu_g \right)^a \left( \mu_g / \rho_g \, D_{AB} \right)^b \left( dp/H \right)^c$$

(38)

In which $K$, $a$, $b$, $c$ are experimentally determined by using Statistical- software Windows version 5.5.

$$Sh = 4.19 * 10^{-2} * \left( G' \, dp / \mu_g \right)^{0.866} \left( \mu_g / \rho_g \, D_{AB} \right)^{0.599} \left( dp/H \right)^{0.850}$$

(39)

Finally the model can be expressed as in the equation:

$$Sh \left( H/dp \right)^{1.2} = 4.19 * 10^{-2} \, Re^{0.87} \, Sc^{0.60}$$

(40)

Correlation coefficient, $R^2 = 0.9838$
Variance explained, $S = 96.789\%$

### 3.2.2. Comparison of the Model with Other Correlation

The proposed model expressed by Equation (40) is compared with Sherwood equation [22];

$$Sh = \beta' \, Re^{0.83} \, Sc^{0.44} \qquad (41)$$

where the $\beta' = 0.021$ to $0.027$ a mean value of $0.023$ is used; The Kramer's equation [23]:

$$Sh = 0.069 \, Re^{0.59} \, Sc^{0.33} \qquad (42)$$

and Weisweiler, *et al.* [32] equation:

$$Sh = 0.3 \, Re^{0.8} \, Sc^{1/3} \left( dp/H \right) \qquad (43)$$

These equations were applied for the operating variables of the present work for acid gas concentration between (100 - 2500) ppm and temperature range (10 - 40)°C. The comparison indicated a reasonable agreement with Kramer's equation while deviated strongly with those obtained by Weisweiler using the Sherwood Equation (41). The absorption rate values obtained in the present work for various acid gases concentrations and tempera- tures were in the range of $0.320 \times 10^{-3}$ - $1.16 \times 10^{-3}$ mol/m$^2$·s. These values compares well with the published data from several investigators using various absorption designs [17,20,24-27]. The details of the comparison can be seen in **Table 5**.

## 4. Conclusions

The following conclusions can be drawn from the present work:

1) The absorption rate of $SO_2$ increases when the temperature of absorbent (urea solution) decreases and increases as the concentration of absorbent solution.

2) The presence of $NO_2$ in the effluent gas stream in addition to $SO_2$ decreases the absorption rate of $SO_2$ in urea solution this may be due to the fast reaction of $NO_2$ with urea as compared with $SO_2$.

**Table 5. Comparison of absorption rate values with some published results.**

| Reference | Acid gas con ppm | TEMP. °C | Absorption rate*$10^{-3}$ mol/m$^2$·s | Contact Pattern |
|---|---|---|---|---|
| Dekker *et al.* (1959) | 250 | 25 | 1.114 | Wetted wall column |
| | 250 | 35 | 1.003 | |
| Kramers *et al.* (1961) | 250 | 20 | 0.77 | Packed bed absorber |
| | 250 | 30 | 0.891 | |
| Kameoka and Pigford (1977) | 250 | 25 | 0.685 | Wetted sphere absorber |
| Weisweiler and Deib (1981) | 250 | 25 | 0.486 | Falling film absorber |
| Lefers and Berg (1982) | 250 | 20 | 0.496 | Wetted wall column |
| | 400 | 20 | 0.182 | |
| Miller (1987) | 670 | 30.3 | 1.562 | Bubble cap plate column |
| | 285 | 38.5 | 1.903 | |
| | 85 | 37.5 | 2.411 | |
| | 580 | 30.8 | 0.826 | Sieve plate column |
| | 390 | 33.2 | 0.871 | |
| | 181 | 32.9 | 1.464 | |
| | 110 | 30.6 | 2.411 | |
| Weisweiler *et al.* (1990) | 150 | 25 | 0.476 | Mixed column |
| | 150 | 35 | 1.394 | |
| | 450 | 25 | 0.105 | |
| | 450 | 35 | 0.333 | |
| | 600 | 25 | 0.018 | |
| This Work | 1500 | 10 | 0.94 | Packed bed |
| | 922.6, 2077 | 16.5 | 0.47, 1.12 | |
| | 1500 | 25 | 0.8412 | |
| | 922.6,2077.6 | 33.6 | 0.42, 1.16 | |
| | 1500 | 40 | 0.722 | |
| | 550 | 10 | 0.338 | |
| | 290, 810 | 16.5 | 0.148, 0.43 | |
| | 550 | 25 | 0.3205 | |
| | 290,810 | 33.6 | 0.1305, 0.381 | |
| | 550 | 40 | 0.269 | |

3) The absorption rate of $NO_2$ decreases at higher urea concentration 0.4 mol/l for low gas concentration ppm due to the decrease the diffusivity of gas.

4) The variables that affect the absorption rates of $SO_2$ and $NO_2$ in urea solution can be formulated using the dimensionless group analysis and may be expressed by the following equation

$$Sh\ (H/dp)^{1.2} = 4.19*10^{-2}\ Re^{0.87}\ Sc^{0.56}$$

This model agrees well with Kramer's Equation (42) with a correlation coefficient, R, of 0.9838.

## 5. Acknowledgements

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