Environment Protection Engineering

Vol. 20 1994 No. 1–4

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MASS TRANSFER RESISTANCE ON THE LIQUID-PHASE SIDE DURING SHORT-TIME LIQUID-TO-GAS EXPOSURE SHOWN BY THE EXAMPLE OF THE ABSORPTION OF SO_2 TO WATER

The absorption of sulphur dioxide to water and aqueous $NaHSO_3$ solutions was studied during a short-time liquid-to-gas exposure ($0.004 < t < 0.035$ s) at a process temperature ranging from 283 to 313 K, in a laminar liquid jet column. The Danckwerts equation was used for calculating the $\beta = f(T)$ relation, which enables evaluation of the liquid-phase side for the sulphur dioxide–water system.

NOTATIONS

$A, A_1, A_2, B, C, E, F, X, Y$ – coefficients,
c_A – concentration of SO_2 in solution, kmol m^{-3},
c_B – concentration of $NaHSO_3$ in solution, kmol m^{-3},
c_E – concentration of HSO_3^- in solution, kmol m^{-3},
c_F – concentration of H^+ in solution, kmol m^{-3},
D_A – liquid-phase diffusivity of SO_2 in solution, m^{2}s^{-1},
D_E – effective diffusivities of HSO_3^- ion in solution, m^{2}s^{-1},
D_F – effective diffusivities of H^+ ion in solution, m^{2}s^{-1},
F_x – fraction of renewal surface,
k_c – mass-transfer coefficient in the liquid phase, ms^{-1},
K – equilibrium constant of reaction (1), kmol m^{-3},
N_A – average rates of absorption of SO_2, kmol m^{-2}s^{-1},
p_{SO_2} – pressure of SO_2, Nm^{-2},
s – fraction of renewal surface per unit time, s^{-1},
t – exposure time of liquid to gas, s,
T – temperature, K,

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β – enhancement factor,
μ – viscosity, kg m^{-1}s^{-1}.

SUPERSCRIPT

* refers to absorption combined with chemical reaction.

SUBSCRIPT

i – refers to interface,
o – refers to bulk of liquid phase.

1. INTRODUCTION

The process of absorption of sulphur dioxide to aqueous solutions has been of considerable interest of many scientists. This interest is mainly due to the increasing environmental hazards (acid rains) which could be brought under control more easily if research on the kinetics of absorption processes of sulphur dioxide was more intensive. For the evaluation of absorption processes – both technological and natural – the knowledge of the value of mass transfer coefficient on the liquid-phase side is important, especially when absorption is accompanied by a chemical reaction in the liquid-phase. Among the methods for determining this coefficient [1], [2], particular attention should be given to the method which employs both the equation describing mass transfer rate in terms of penetration theory and measurements of absorption obtained in tests on laboratory model absorbers [3], [4]. This method also enables us to determine the values of the factor of absorption kinetics enhancement which is affected by the chemical reaction in the liquid phase.

The kinetics of absorption of sulphur dioxide to water has been investigated, e.g., by BEILKE and LAMB [5], HIKITA et al. [6], as well as CARMICHAEL and PETERS [7]. However, analyzing the data reported there, it becomes obvious that there is no agreement on the form of the $\beta = f$(physicochemical parameters of the process) and on the lack of some physicochemical constants (which should be included in calculations). Because of those drawbacks, the application of those results to calculations raises certain problems.

It is worth noting that the results reported by HIKITA et al. [6] are very interesting. On analyzing the absorption of sulphur dioxide into water, they assumed that the reaction

$$SO_2 + H_2O \leftrightarrows HSO_3^- + H^+ \tag{1}$$

is a reversible reaction of the type $A \leftrightarrows E + F$. Defining the absorption rate in terms of the penetration theory

$$N_A^* = \beta 2\sqrt{D_A/\pi t}(c_{Ai} - c_{Ao}), \tag{2}$$

they gave the following formula which enabled calculation of the enhancement factor

$$\beta = 1 + \frac{\sqrt{D_E/D_A}}{2(c_{Ai} - c_{Ao})}\left[\sqrt{(c_{Eo} + c_{Fo}\sqrt{D_F/D_E})^2 + 4K\sqrt{D_F/D_E}(c_{Ai} - c_{Ao})}\right.$$
$$\left. - (c_{Eo} + c_{Fo}\sqrt{D_F/D_E})\right]. \tag{3}$$

When $D_E = D_F$ and $c_{Eo} = c_{Fo}$, equation (3) may be reduced to the form

$$\beta = 1 + \sqrt{D_E/D_A}\frac{\sqrt{K}}{\sqrt{c_{Ai}} + \sqrt{c_{Ao}}}. \tag{4}$$

The relations obtained via the above route were verified experimentally by measuring the absorption rate of sulphur dioxide to water. HIKITA et al. [6] made use of an absorber with wetted walls. The time of liquid-to-gas exposure varied from 0.049 to 0.97 s. The experiments were conducted at atmospheric pressure and a temperature ranging from 288 to 318 K. And it is for that particular case that they have anticipated $D_E/D_A = D_F/D_A = 1.32$; $c_{Ao} = 0$. The remaining process parameters are listed in table 1.

Table 1

Physicochemical constants of the SO_2–H_2O system [6]

T [K]	c_{Ai} [kmol/m^3]	$D_A \times 10^9$ [m^2/s]	$K \times 10^2$ [kmol/m^3]
288	1.64	1.34	2.19
298	1.16	1.76	1.70
308	0.831	2.25	1.31
318	0.595	2.81	0.991

Sulphur removal from industrial gases often involves high-velocity scrubbers (e.g. of the Venturi type) with very short times of liquid-to-gas exposure. In low-velocity absorbers, it is the absorption in the liquid jet zone that plays a significant role (note that this absorption also occurs within a very short time). It has been found that this part of the mass transfer process has a substantial contribution to treatment effect. The times of exposures are generally much shorter than those reported by HIKITA et al. [6], so the processes that occur in these short exposure times are still far from being well understood.

The objective of this study was to verify the results reported in the literature under modified conditions, i.e., at exposure times t shorter than 0.049 s and with a laminar liquid jet absorber.

2. EXPERIMENTAL APPARATUS AND MEASURING TECHNIQUE

The study of kinetics of absorption involves a wide variety of model absorbers. Four major types can be listed here: wetted-wall absorbers, rotating-drum absorbers, laminar liquid jet columns, and disk columns [3], [4]. Of these, the laminar liquid jet column seemed to be best suited for our study. Apart from the fact that absorbers of that kind are really popular, they have advantage of creating experimental conditions which comply quite well with the assumptions of theoretical models.

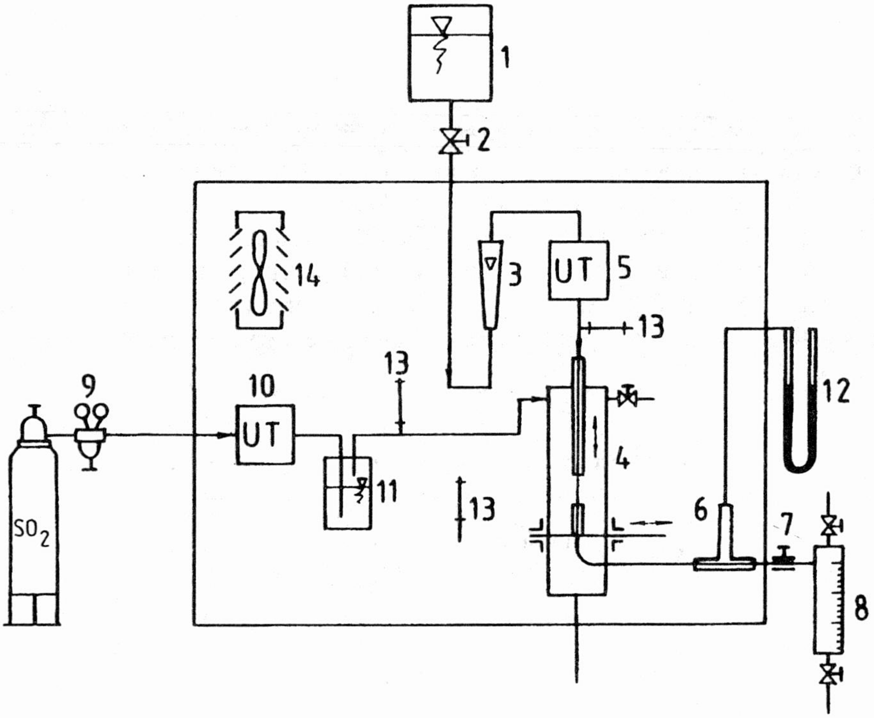

Fig. 1. Experimental setup

The experimental system is shown in figure 1. The sorbing solution moved by gravitation from tank (*1*) (through a control valve (*2*) and a rotameter (*3*)) to the nozzle of the absorber (*4*). The temperature of the solution was established by an ultrathermostat (*5*). Then the solution entered a glass capillary. From there, it passed through a T-pipe with a capillary (*6*) and a flow regulator (*7*) to enter a burette (*8*) where volumetric flow rate was measured and samples for analysis were taken. Sulphur dioxide (supplied from a cylinder) moved through a control valve (*9*), an ultrathermostat (*10*) and humidifier (*11*) to be passed to the interior of the absorber (*4*). There the sulphur dioxide stream flowed cocurrently to the laminar liquid jet to leave the absorber. Pressure in the column (in the relation to the atmospheric pressure) was measured by means of a U-pipe (*12*) filled up with water. Thermometers (*13*) were used for measuring the temperatures of the sulphur dioxide both in the sorbing solution and in the thermostated tank (*14*).

The nozzle of the experimental absorber had a diameter of 1.2 mm. The contraction coefficient had been evaluated by the photographic method and was determined to be 0.82, which corresponded to the value reported by DRAMIŃSKI and KAWECKI [8].

The quantity of absorbed sulphur dioxide was measured iodometrically.

3. RESULTS

Making use of the Higbie model, mass transfer in a laminar liquid jet column can be written as

$$N_A = k_c(c_{Ai} - c_{Ao}) \tag{5}$$

where

$$k_c = 2\sqrt{D_A/\pi t}. \tag{6}$$

When a chemical reaction occurs in the liquid phase

$$N_A^* = k_c^*(c_{Ai} - c_{Ao}) \tag{7}$$

where

$$k_c^* = \beta k_c. \tag{8}$$

Thus, measuring the density of the diffusing mass stream (N_A^*) and assuming that the concentration of the diffusing gas in the bulk of the liquid phase (c_{Ao}) equals zero, we can find the enhancement factor

$$\beta = k_c^*/k_c = (N_A^*/c_{Ai})/2\sqrt{(D_A/\pi t)}. \tag{9}$$

About 300 measurements were carried out for the sulphur dioxide–water system at a process temperature (T) between 293 and 313 K and a time of liquid-to-gas exposure (t) ranging from 0.004 to 0.035 s. Exposure time was varied by changing both the jet length and the rate of water flow through the absorber.

The results are plotted in figure 2 in the form of $k_c = f(t^{-0.5})$. The solid line is described by equation (6), whereas the dashed line corresponds with the following equation:

$$k_c^* = \beta A_1 t^{-0.402}\sqrt{D_A}. \tag{10}$$

Experimental data is represented by the points of coordinates (N_A^*/c_{Ai}, $t^{-0.5}$). As shown by these plots, the measured results of the kinetics of sorption in the investigated range of exposure time are not well correlated with the Higbie equation which is generally applied to laminar liquid jet absorbers. Hence, attempts were made to improve this correlation in terms of the Danckwerts equation. Thus, the kinetics of absorption becomes

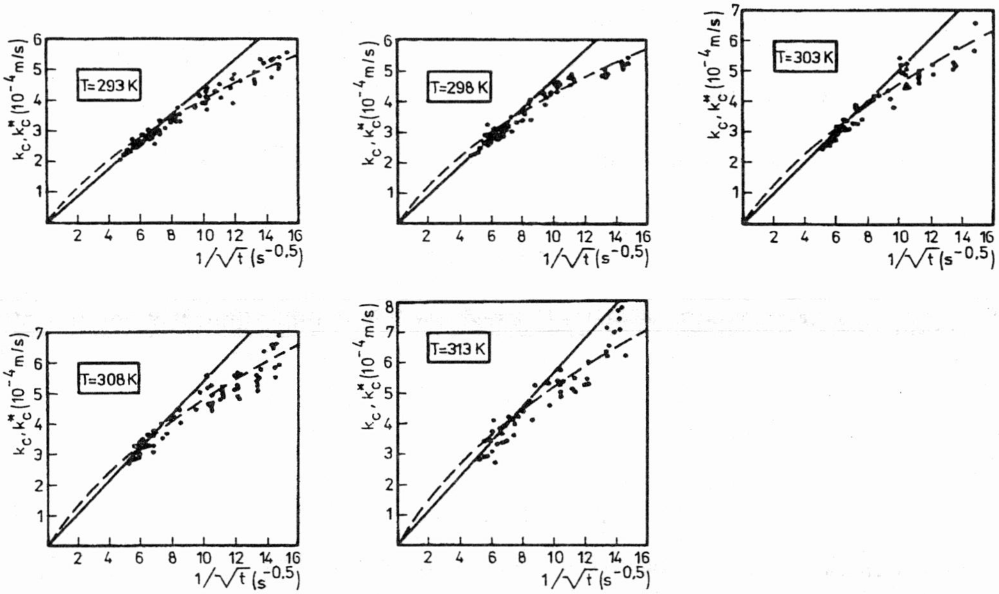

Fig. 2. Results of SO_2 absorption in water: the Higbie model

$$N_A^* = \beta\sqrt{D_A s}(c_{Ai} - c_{Ac}). \tag{11}$$

There appeared the need to determine such a function that would describe the hydrodynamics of the process in terms of the Danckwerts model: $\sqrt{s} = f$ (hydrodynamic parameters of the process).

In this paper, the above function was established by measuring the kinetics of physical absorption in a laminar liquid jet absorber, wherein sulphur dioxide was absorbed to aqueous solutions of $NaHSO_3$. The concentration of $NaHSO_3$ (c_B) in the water, the temperature (T) of the process and the time of exposure (t) were equal to 0.05 kmol/m^3, 293–313 K and 0.004–0.030 s, respectively. Diffusivity (D_A) was determined experimentally, making use of the diffusivity value for sulphur dioxide in the $NaHSO_3$ solution reported by HIKITA et al. [9] for $T = 298$ K and taking into account the following relation:

$$D_2 = D_1 \mu_1 T_2 / \mu_2 T_1 . \tag{12}$$

The coefficient of viscosity (μ) for aqueous solutions of $NaHSO_3$ was measured in a Hopler-type viscosimeter.

The following procedures were adopted to the interpretation of approximately 120 measurements pertaining to the kinetics of absorption:

mass transfer in the laminar liquid jet absorber was described in terms of the Danckwerts equation (11) at $c_{Ao} = 0$, $\beta = 1$;

the assumption that function $\sqrt{s} = f(t)$ is defined by the empirical relation

$$\sqrt{s} = A_1 t^B \tag{13}$$

and by

$$c_{Ai} = A_2 p^c_{SO_2} T^E \exp Fc_B \tag{14}$$

allowed us to obtain the following relation (after having combined (11), (13) and (14)):

$$N_A/\sqrt{D_A} = At^B p^C_{SO_2} T^E \exp Fc_B \tag{15}$$

where

$$A = A_1 A_2 . \tag{16}$$

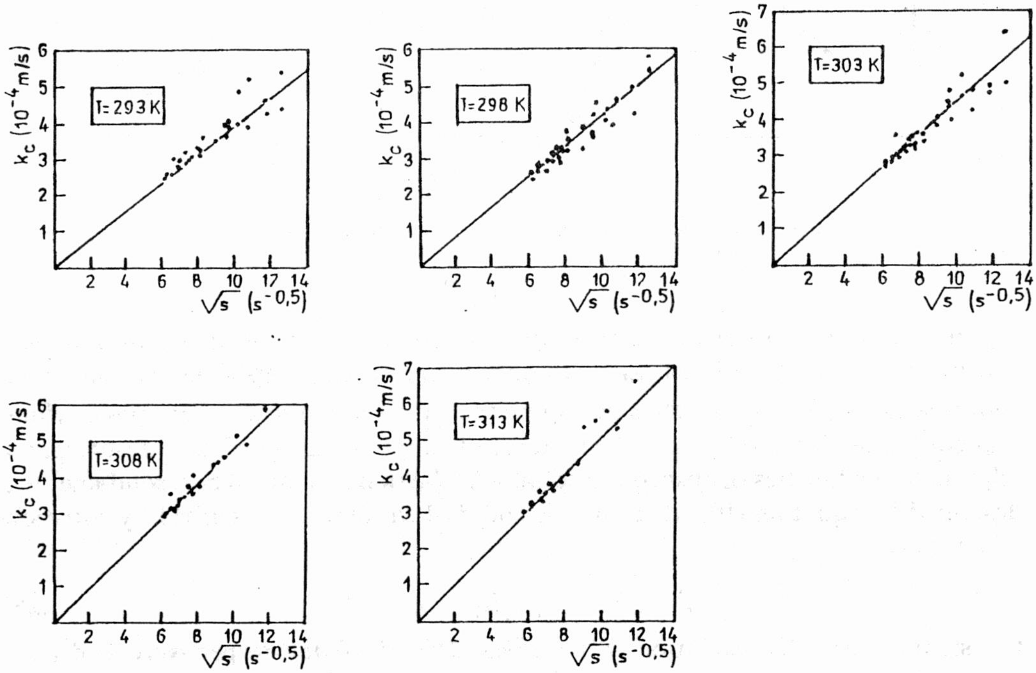

Fig. 3. Results of SO_2 absorption in aqueous solution of $NaHSO_3$: the Danckwerts model

Based on the measured values of N_A, t, p_{SO_2} and T, the constants in equation (15) were calculated by means of the multiple linear regression method; hence $A = \exp 21.005$, $B = -0.402$, $C = 3.856$, $E = -7.931$, $F = -14.374$. Furthermore, making use of the results measured at $T =$ 298 K as well as of the c_{Ai} value which is known for that temperature (HIKITA et al. [9]), the value of the A_2 constant was established in terms of equation (14). Thus, it was easy to calculate A_1 using equation (16). In the measured range, $A_1 = 1.454$. Hence

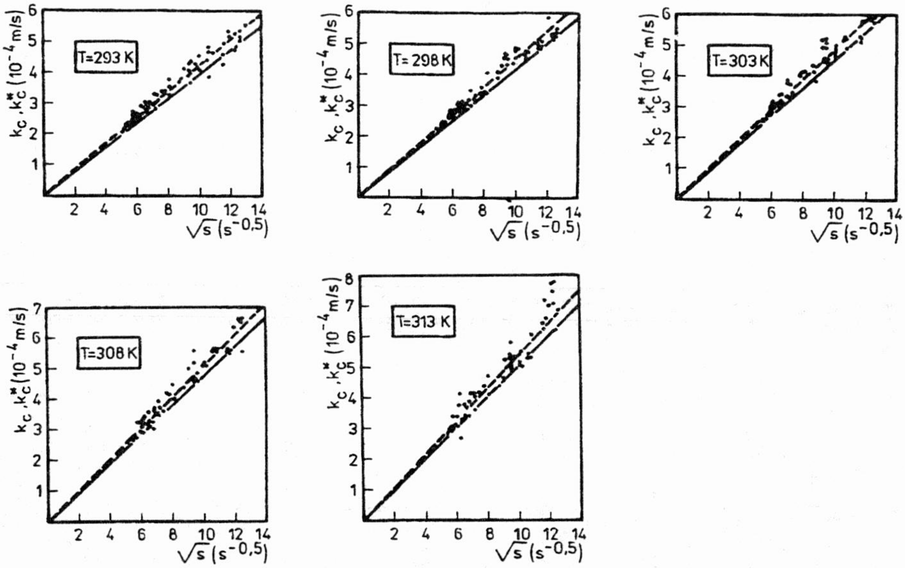

Fig. 4. Results of SO_2 absorption in water: the Danckwerts model

$$\sqrt{s} = 1.454\ t^{-0.402}. \tag{17}$$

Figure 3 gives relevant plots and their analysis. Solid lines are described by equation (10) where $\beta = 1$, $A_1 = 1.454$, and the points representing experimental data have coordinates $(N_A/c_{Ai}, \sqrt{s})$. When analyzing the curves in figure 4, it becomes obvious that equations (10) and (11) may be used for the approximation of the measurements relating to the kinetics of absorption of sulphur dioxide to water. Thus, solid lines are described by equation (10) where $\beta = 1$, and dashed lines are described by equation (10) where

$$\beta = N_A^*/(c_{Ai}\sqrt{D_A s}) = XT^Y. \tag{18}$$

Constants X and Y in equation (18) equal 1.135 and -0.011, respectively, and have been determined by multiple linear regression method. The points representing experimental data have coordinates $(N_A/c_{Ai}, \sqrt{s})$.

Let us now compare the model proposed by Higbie (describing hydrodynamics of our experimental system) with that proposed by Danckwerts. Thus, we have

$$(N_A/(c_{Ai}\sqrt{D_A})^2 = 4/\pi t \tag{19}$$

and

$$s = (N_{Ai}/c_{Ai}\sqrt{D_A})^2 = 2.113\ t^{-0.804}, \tag{20}$$

respectively. Both models are plotted in figure 5 (solid lines). The points of coordinates (s, t) represent the experimental data obtained in our study. As shown by

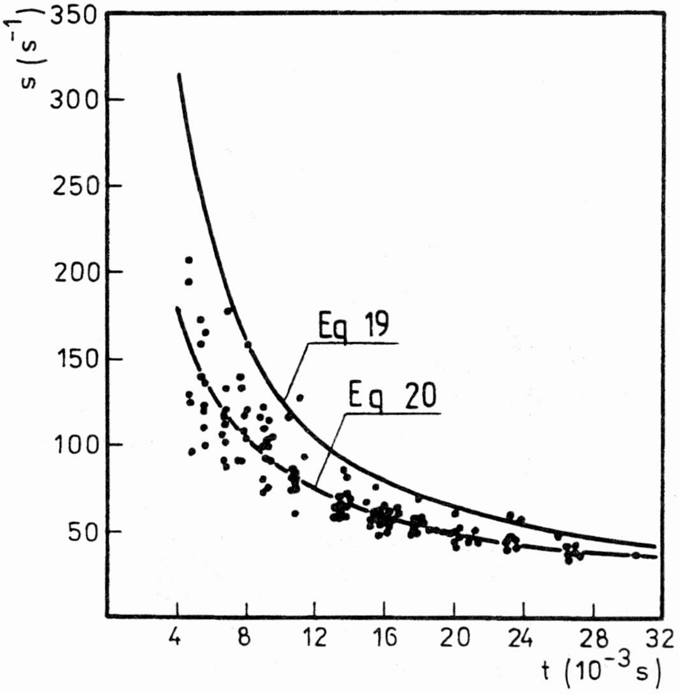

Fig. 5. Comparison of the Higbie and Danckwerts models of physical absorption. Absorption of SO_2 in aqueous solution of $NaHSO_3$ ($T = 293$–313 K)

these plots, the Danckwerts equation describes better the hydrodynamics of the system, provided that the time of liquid-to-gas exposure (t) ranges from 0 to 0.030 s. When $t > 0.030$ s, we may expect that the models will yield consistent results.

Taking into account the definition of the terms s (a fraction of reneval surface F_X per unit time) we have

$$s = F_x/t, \tag{21}$$

hence

$$F_x = st. \tag{22}$$

Thus, for the Danckwerts model we obtain

$$F_X^D = 2.113t^{0.196}. \tag{23}$$

But if we were to interpret equation (19) in terms of the Higbie model, we would have

$$F_X^H = 4/\pi. \tag{24}$$

The plots illustrating equations (23) and (24) are shown in figure 6. The case described by equation (24) is such that irrespectively of the time of liquid-to-gas exposure (t), the fraction of the reneval surface within this period is constant and

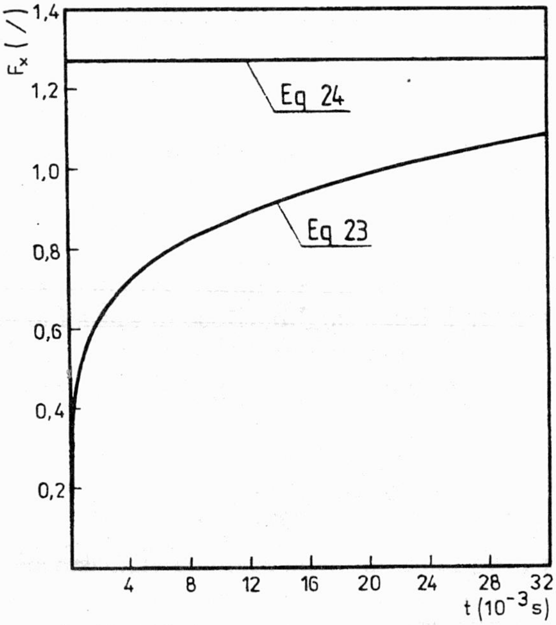

Fig. 6. Comparison of two Higbie and Danckwerts models of physical absorption

equal to $F_X^H = 4/\pi$. In the case described by equation (23), F_X^D is a fraction of t (the longer the time of exposure, the greater the fraction of the renewal surface). Hence, the Danckwerts model seems to be better than that of Higbie for describing the physical sense of the process that occurs in the laminar liquid jet absorber.

4. CONCLUSIONS

Laboratory tests of the absorption of sulphur dioxide to water and aqueous $NaHSO_3$ solutions in a laminar liquid jet absorber at short times of liquid-to-gas exposure ($0.004 < t < 0.030$ s) have shown that the measured results are well described by the Danckwerts equation.

A relation describing the hydrodynamics of the system ($\sqrt{s} = 1.454 t^{-0.0402}$) as well as a function enabling the calculation of the enhancement factor ($\beta = 1.135 T^{-0.011}$) for the sulphur dioxide–water system and the process temperature range $T = 293$–313 K have been determined. The values of the enhancement factor (β) calculated via this procedure are some 7% lower than those calculated in terms of HIKITA et al. [6] procedure.

There are two major factors that may have contributed to this difference: first, a wall effect on the liquid film turbulence due to the velocity gradient (since HIKITA et al. [6] made use of a wetted-wall column), and second, some unavoidable measuring and analytical errors.

REFERENCES

[1] Pohorecki R., *Zastosowanie modeli penetracyjnych wnikania masy do badania i projektowania procesów absorpcji z reakcją chemiczną*. Część I. *Rozwiązania teoretyczne i ograniczenia*, Inż. i Ap. Chem., 1971, 5, 13–17.

[2] Pohorecki R., *Zastosowanie modeli penetracyjnych wnikania masy do badania i projektowania procesów absorpcji z reakcją chemiczną*. Część II. *Metody projektowania i badania absorberów*, Inż. i Ap. Chem., 1971, 6, 18–21.

[3] Danckwerts P.V., *Gas Liquid Reactions*, New York, McGraw-Hill, 1970.

[4] Charpentier J.C., *Les ecoulements gaz–liquide en genie chimique*, La Houille Blanche, 1979, 6/7, 419–425.

[5] Beilke S., Lamb D., *Remarks of the Rate of Formation of Bisulfite Ions in Aqueous Solution*, A.I.Ch.E.J., 1975, 21, 402–404.

[6] Hikita H., Asai S., Nose H., *Absorption of Sulphur Dioxide into Water*, A.I.Ch.E.J., 1978, 24, 147–149.

[7] Carmichael G.R., Peters K.L., *Some Aspects of* SO_2 *Absorption by Water-Generalized Treatment*, Atmos. Environ., 1979, 13, 1505–1513.

[8] Draminński M., Kawecki W., *Stabilność laminarnego strumienia cieczy stosowanego do badania absorpcji gazów*, Inż. Chem., 1975, V, 235–242.

[9] Hikita H., Asai S., Tsuji T., *Absorption of Sulphur Dioxide into Aqueous Sodium Hydroxide and Sodium Sulfite Solutions*, A.I.Ch.E.J., 1977, 23, 538–544.

BADANIA OPORÓW WNIKANIA MASY PO STRONIE FAZY CIEKŁEJ PRZY KRÓTKICH CZASACH KONTAKTU FAZ NA PRZYKŁADZIE ABSORPCJI SO_2 W WODZIE

Badano absorpcję dwutlenku siarki w wodzie i wodnych roztworach $NaHSO_3$ przy krótkich czasach kontaktu faz ($0{,}004 < t < 0{,}035$ s), w zakresie zmienności temperatury procesu $T = 283$–313 K, w absorberze z laminarnym strumieniem cieczy. Na podstawie równania Danckwertsa wyznaczono zależność $\beta = f(T)$, umożliwiającą określanie wartości współczynnika wnikania masy po stronie fazy ciekłej dla układu dwutlenek siarki–woda.

ИССЛЕДОВАНИЯ СОПРОТИВЛЕНИЙ ПРОНИКНОВЕНИЯ МАССЫ В СТОРОНЕ ЖИДКОЙ ФАЗЫ ПРИ КОРОТКИХ ВРЕМЕНАХ КОНТАКТА ФАЗ НА ПРИМЕРЕ АБСОРБЦИИ SO_2 В ВОДЕ

Исследована абсорбция двуокиси серы в воде и водных растворах $NaHSO_3$ при коротких временах контакта фаз ($0{,}004 < t < 0{,}035$ сек.) в пределах изменчивости температуры процесса $T = 283$–313 K, в абсорбере с ламинарным потоком жидкости. На основе уравнения Данквертса определена зависимость $\beta = f(T)$, дающая возможность определения значения коэффициента проникновения массы в стороне жидкой фазы для системы двуокись серы–вода.