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On the SO_2 Problem in Thermal Power Plants. 2.Two-steps chemical absorption modeling

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Abstract: The modeling of the gas absorption in a new column apparatus for waste gases purification from SO_2, using two-phase absorbent ($CaCO_3$ / H_2O suspension) is presented. The process is realized in a three-zone column. In the upper zone a physical absorption in gas-liquid drops system is realized and the big convective transfer in the gas phase leads to a decrease of the mass transfer resistances in this phase. In the middle zone a chemical absorption in liquid-gas bubbles system takes place and the big convective transfer in the liquid phase leads to a decrease of the mass transfer resistances in this phase. The large volume of the liquid in the middle zone causes an increase of the chemical reaction time and as a result a further decrease of the mass transfer resistances in the liquid phases is realized. The third zone is the column tank, where the chemical reaction takes place only.

Keywords: absorption, gas purification, two-phase absorbent method, three-zone column, convection-diffusion model, average concentration model.

Introduction

In the first part of the paper [1] was shown, that in the cases of waste gases purification from SO_2, using two-phase absorbent ($CaCO_3/H_2O$ suspension) from some companies (Babcock & Wilcox Power Generation Group, Inc., Alstom Power Italy, Idreco-Insigma-Consortium) in the thermal power plants, the interphase mass transfer process in the gas-liquid drops system is practically physical absorption as a result of the low concentration of the dissolved SO_2 and $CaCO_3$ in the water. In these conditions the mass transfer resistances in the gas and liquid phases are $R_1 = 0.44$ and $R_2 = 0.56$, respectively, i.e. absorption intensification must be realized by convective mass transfer in the gas phase (in gas-liquid drops system) and in the liquid phase (liquid-gas bubbles system). This theoretical result is possible to be realized in a three-zone column. In the upper zone a physical absorption in gas-liquid drops system is realized and the big convective transfer in the gas phase leads to a decrease of the mass transfer resistances in this phase. In the middle zone a chemical absorption in liquid-gas bubbles system takes place and the big convective transfer in the liquid phase leads to a decrease of the mass transfer resistances in this phase. The large volume of the liquid in the middle zone causes an increase of the chemical reaction time and as a result a further decrease of the mass transfer resistances in the liquid phases is realized. The third zone is the column tank, where the chemical reaction takes place only. This idea is realized [2] in an absorption column (Fig.1) with two absorption zones.

The apparatus comprises a cylindrical absorption column 1, fitted at its lower end with an inlet 2 for submission of waste gases. Above the bottom of the absorption column 1 is placed in a horizontal gas distribution plate 3 (bell plate or any other device providing the cleansing bubbling gas through the absorbent in the middle part of the column) so that between it and the bottom of absorption column 1 is shaped entrance area of the input gas. On the distribution plate 3 are installed vertical distribution pipes 4 at the middle of the column 1, the number of which depends on the gas delivery. Each of the gas distribution pipes 4 is covered with concentric bubbling cap 5, which lies on plate 3 and has slots 6 at the bottom. Between the distribution pipes 4 and the bubbling caps 5 are formed passages 7, which are open to the pipes 4. The volume between the pipes 4 is filled with absorbent suspension.

The upper part of the absorption column 1 is equipped with sprinklers system 9, which is located above the drop separator 10 and outlet 11, provided for the purified gas. Exits 8 (of bubbling area) are associated with tank 12 through pipe 13. The level of the absorbent in the bubbling zone is controlled by the turn-cock 20. The tank 12 is provided with the turn-cock 19. System sprinklers 9 are connected by circulation pipes 15 and 16 and circulation pump 18 with the tank 12.

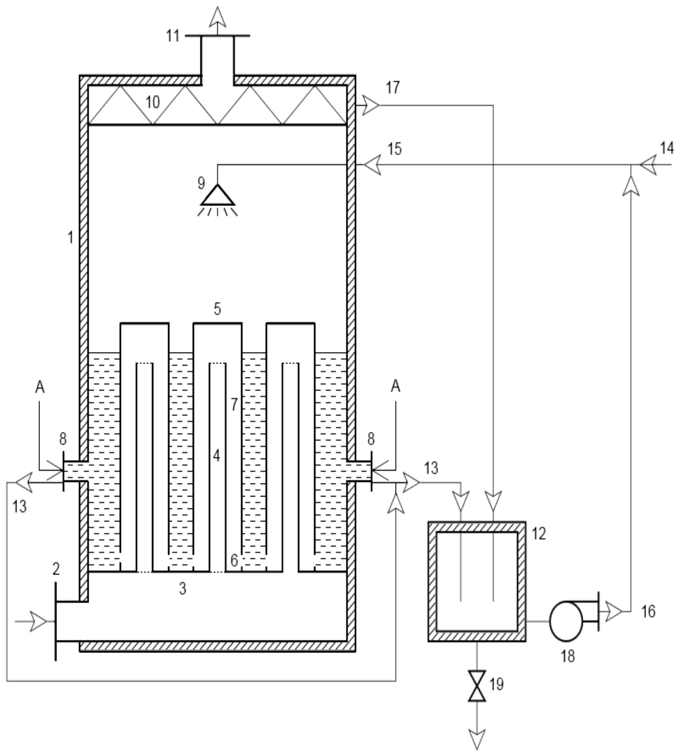

Fig.1

A tangential inlet 2 of the gas phase [3] leads to a significant decrease of the velocity radial non-uniformity below the gas distribution plate 3. This effect increases after gas distribution in the pipes 4 and as a result the mass transfer rate in the gas phase increases [4-8].

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The sprinklers system 9 leads to the decrease of the velocity radial non-uniformity in the liquid phase and as a result the mass transfer rate in the liquid phase increases too.

1. Physical absorption modeling in the upper zone

Let's consider the absorption column of Fig. 1 with a diameter D [m], where l_1 [m] is the height of the upper zone between bubbling caps 5 and sprinklers system 9 (gas-liquid drops system zone) and l_2 [m] is the height of the middle (liquid-gas bubbles system) zone between distribution plate 3 and the liquid surface (practically the bubbling caps 5 height). The diameter of the gas distribution pipes 4 is D_0 [m], the bubbling caps 5 diameter is D_1 [m] and n is its number. The gas and liquid flow rates in the column are Q_{G} and Q_{L} [m^3.s^{-1}], the inlet velocities in the gas and liquid phases are u_{G}^0 and u_{L}^0 [m.s^{-1}] and ε_{G}, ε_{L} $\left(\varepsilon_{\mathrm{G}}+\varepsilon_{\mathrm{L}}=1\right)$ are hold-up coefficients, respectively:

$$u_{\mathrm{G}}^0=\frac{Q_{\mathrm{G}}}{F},\quad u_{\mathrm{L}}^0=\frac{Q_{\mathrm{L}}}{F},\quad F=\frac{\pi D^2}{4},\qquad \varepsilon_{\mathrm{G}}=\frac{Q_{\mathrm{G}}}{Q_{\mathrm{G}}+Q_{\mathrm{L}}},\quad \varepsilon_{\mathrm{L}}=\frac{Q_{\mathrm{L}}}{Q_{\mathrm{G}}+Q_{\mathrm{L}}}. \tag{1}$$

The absorber working volume W [m^3] in the middle zone is:

$$W=\left(F-nF_1\right)l_2,\quad F_1=\frac{\pi D_1^2}{4}. \tag{2}$$

Let's consider the physical absorption in gas-liquid drops system [1] in the upper zone of the column (Fig. 1), where the radial non-uniformities of the velocities distributions in the gas and liquid phases absent, practically. This is a result [3] of the tangential inlet 2 of the gas phase in the column 1, the gas distribution pipes 4 in the middle column zone and the sprinklers system 9 in the upper column zone. In these conditions the radial non-uniformities of the concentrations distributions in the gas and liquid phases absent too and is possible to be used average concentrations values over the cross-sectional area of the column.

In the upper zone a convection-diffusion model [1, 4, 5] is possible to be used for a counter-current absorption process in two cylindrical coordinates systems - $\left(z_1,r\right)$, $\left(z_2,r\right)$, $\left(z_1+z_2=l_1\right)$, where $\bar{c}_{\mathrm{G}}=\bar{c}_{\mathrm{G}}\left(z_1\right)$ and $\bar{c}_{\mathrm{L}}=\bar{c}_{\mathrm{L}}\left(z_2\right)$ are the axial distributions of the average SO_2 concentrations in the gas and liquid phases:

$$\begin{aligned}
&\omega_{\mathrm{G}}u_{\mathrm{G}}^0\frac{d\,\bar{c}_{\mathrm{G}}}{dz_1}=\omega_{\mathrm{G}}D_{\mathrm{G}}\frac{d^2\bar{c}_{\mathrm{G}}}{dz_1^2}-k\left(\bar{c}_{\mathrm{G}}-\chi\bar{c}_{\mathrm{L}}\right);\\
&z_1=0,\quad \bar{c}_{\mathrm{G}}=c_{\mathrm{G}}^0,\quad \left(\frac{d\,\bar{c}_{\mathrm{G}}}{dz_1}\right)_{z_1=0}=0;\\
&\omega_{\mathrm{L}}u_{\mathrm{L}}^0\frac{d\,\bar{c}_{\mathrm{L}}}{dz_2}=\omega_{\mathrm{L}}D_{\mathrm{L}}\frac{d^2\bar{c}_{\mathrm{L}}}{dz_2^2}+k\left(\bar{c}_{\mathrm{G}}-\chi\bar{c}_{\mathrm{L}}\right);\\
&z_2=0,\quad \bar{c}_{\mathrm{L}}=0,\quad \left(\frac{d\,\bar{c}_{\mathrm{L}}}{dz_2}\right)_{z_2=0}=0,
\end{aligned} \tag{3}$$

where c_{G}^0 is the inlet concentration of SO_2 in the gas phases, equal to the outlet SO_2 concentration in the gas phase from the middle zone ($\bar{c}_1\left(l_2\right)$), χ is the Henry's number.

2. Chemical absorption modeling in the middle zone

The gas bubbling in the absorbent volume W in the middle zone creates an ideal mixing regime and as a result the concentrations [kg-mol.m^{-3}] of SO_2 ($\bar{c}_2$) and $CaCO_3$ ($\bar{c}_3$) in the liquid phase are constants, where $\bar{c}_3$ is practically the maximal (equilibrium) solubility of $CaCO_3$ in water.

The mass flow rates [kg-mol.s^{-1}] of SO_2 at the inlet 2 and outlet 11 of the column are $Q_{\mathrm{G}}c_1^0$ and $Q_{\mathrm{G}}c_{\mathrm{G}}\left(l_1\right)$, where c_1^0 and $c_{\mathrm{G}}\left(l_1\right)$ are the SO_2 concentrations (kg-mol.m^{-3}) in the input and output gas flow. The difference between them is the SO_2 absorption rate V_1 [kg-mol.s^{-1}] in the column:

$$V_1=Q_{\mathrm{G}}\left[c_1^0-\bar{c}_{\mathrm{G}}\left(l_1\right)\right]. \tag{4}$$

The chemical reaction rate V_2 [kg-mol.m^{-3}.s^{-1}] between SO_2 and $CaCO_3$ in the middle zone is possible to be presented as:

$$V_2=k_0\bar{c}_2\bar{c}_3, \tag{5}$$

where k_0 is the chemical reaction rate constant.

The concentration of SO_2 ($\bar{c}_2$) in the liquid phase in the middle zone is a constant if the SO_2 absorption rate V_1 in the column is equal to the amount of SO_2 (V_2W), reacts chemically with $CaCO_3$ in the middle zone, i.e.

$$\bar{c}_2=\frac{Q_{\mathrm{G}}\left[c_1^0-\bar{c}_{\mathrm{G}}\left(l_1\right)\right]}{Wk_0\bar{c}_3}. \tag{6}$$

The axial distributions $\bar{c}_1\left(z\right)$ of the average SO_2 concentration in the gas phases in the middle zone is possible to be obtained as a solution of the problem:

$$\begin{aligned}
&\bar{u}_1\frac{d\,\bar{c}_1}{dz}=D_{\mathrm{G}}\frac{d^2\bar{c}_1}{dz^2}-k_1\left(\bar{c}_1-\chi\bar{c}_2\right);\\
&z=0,\quad \bar{c}_1=c_1^0,\quad \left(\frac{d\,\bar{c}_1}{dz}\right)_{z=0}=0;
\end{aligned} \tag{7}$$

where k_1 (s^{-1}) is the interphase mass transfer coefficient in the liquid-gas bubbles zone.

The mathematical model of the SO_2 absorption, using two-phase absorbent ($CaCO_3/H_2O$ suspension), in the column 1 on the Fig.1 is the set of equations (3), (6), (7), where $c_{\mathrm{G}}^0=\bar{c}_1\left(l_2\right)$. The quantitative description of the process needs the model's generalized (dimensionless) variables.

3. Generalized (dimensionless) variables model

The maximal values of the variables will be used as scales in the generalized variables:

$$Z = \frac{z}{l_2}, \quad Z_1 = \frac{z_1}{l_1}, \quad Z_2 = \frac{z_2}{l_1}, \quad C_G = \frac{\bar{c}_G}{c_1^0},$$
$$C_L = \frac{\bar{c}_L \chi}{c_1^0}, \quad C_1 = \frac{\bar{c}_1}{c_1^0}, \quad C_G^0 = \frac{c_G^0}{c_1^0}, \quad C_2 = \frac{\bar{c}_2 \chi}{c_1^0}. \tag{8}$$

If put (8) in equations (3), (6), (7), the model of SO_2 absorption in a three-zone column has the form:

$$\frac{dC_G}{dZ_1} = \mathrm{Pe}_G^{-1} \frac{d^2 C_G}{dZ_1^2} - K_G (C_G - C_L);$$
$$Z_1 = 0, \quad C_G = C_G^0 = C_1(1), \quad \left(\frac{dC_G}{dZ_1}\right)_{Z_1=0} = 0. \tag{9}$$

$$\frac{dC_L}{dZ_2} = \mathrm{Pe}_L^{-1} \frac{d^2 C_L}{dZ_2^2} + K_L (C_G - C_L);$$
$$Z_2 = 0, \quad C_L = 0, \quad \left(\frac{dC_L}{dZ_2}\right)_{Z_2=0} = 0. \tag{10}$$

$$\frac{dC_1}{dZ} = \mathrm{Pe}^{-1} \frac{d^2 C_1}{dZ^2} - K (C_1 - C_2);$$
$$Z = 0, \quad C_1 = 1, \quad \left(\frac{dC_1}{dZ}\right)_{Z=0} = 0. \tag{11}$$

$$C_2 = \frac{Q_G \left[1 - C_G(1)\right] \chi}{W k_0 \bar{c}_3}. \tag{12}$$

In (9)-(12) are used the next dimensionless parameters:

$$\mathrm{Pe}_G = \frac{u_G^0 l_1}{D_G}, \quad \mathrm{Pe}_L = \frac{u_L^0 l_1}{D_L}, \quad \mathrm{Pe} = \frac{\bar{u}_1 l_2}{D_G},$$
$$K_G = \frac{k l_1}{\omega_G u_G^0}, \quad K_L = \frac{k l_1 \chi}{\omega_L u_L^0}, \quad K = \frac{k_1 l_2}{\bar{u}_1}. \tag{13}$$

4. Industrial conditions

Let's consider (Fig.1) an industrial absorption column 1 with a diameter D = 18.2 [m], where l_1 = 6.9 [m] is the height of the upper zone between bubbling caps 5 and sprinklers system 9 (gas-liquid drops system zone) and l_2 = 1 m is the height of the middle (liquid-gas bubbles system) zone between distribution plate 3 and the liquid surface (practically the bubbling caps 5 height). The absorption process is characterized by the average gas velocity $u_G^0 = 4.14$ [m.s^{-1}], average liquid drops velocity $u_L^0 = 3.75$ [m.s^{-1}] (during the existence of the drops 1.8 [s]), inlet SO_2 concentration in the gas phase $c_1^0 = 10^{-4}$ [kg-mol.m^{-3}], inlet SO_2 concentration in the liquid phase $\bar{c}_L = 0$ [kg-mol.m^{-3}], liquid [m^3.s^{-1}] / gas [m^3.s^{-1}] ratio $\mathrm{L/G} = 0.02$ ($\omega_G = 0.98$, $\omega_L = 0.02$), Henry's number $\chi = 2.55.10^{-2}$, diffusivity of SO_2 in the gas (air) $D_1 = 1.03.10^{-5}$ [m^2.s^{-1}] and liquid (water) $D_2 = 1.67.10^{-9}$ [m^2.s^{-1}] phases. The desired absorption degree will be 94%.

From presented industrial conditions and (13) follows:

$$\mathrm{Pe}_G = 2.77.10^6, \quad \mathrm{Pe}_L = 1.55.10^{10},$$
$$\mathrm{Pe} = 0.40.10^6, \quad \frac{K_G}{K_L} = \frac{\omega_L u_L^0}{\omega_G u_G^0} = 0.725 \tag{14}$$

and the model (9)-(12) has a convective form:

$$\frac{dC_G}{dZ_1} = -K_G (C_G - C_L); \quad Z_1 = 0, \quad C_G = C_G^0 = C_1(1). \tag{15}$$

$$\frac{dC_L}{dZ_2} = 1.379 K_G (C_G - C_L); \quad Z_2 = 0, \quad C_L = 0. \tag{16}$$

$$\frac{dC_1}{dZ} = -K (C_1 - C_2); \quad Z = 0, \quad C_1 = 1. \tag{17}$$

$$C_2 = \frac{Q_G \left[1 - C_G(1)\right] \chi}{W k_0 \bar{c}_3}. \tag{18}$$

4. Algorithm for model equation solution

4.1. Upper zone model

The solution of the model equations of the upper zone uses the next iterative Algorithm I:

1. Solution of the problem

$$\frac{dC_G^0}{dZ_1} = -K_G C_G^0; \quad Z_1 = 0, \quad C_G^0 \equiv 1. \tag{19}$$

2. Presentation of C_G^0 as a polynomial $C_G^0 = a_0^0 + a_1^0 Z_1 + a_2^0 Z_1^2$.

3. Solution of the problem

$$\frac{dC_L^s}{dZ_2} = 1.34 K_G \left[a_0^{(s-1)} + a_1^{(s-1)}(1 - Z_2) + a_2^{(s-1)}(1 - Z_2)^2 - C_L^s\right],$$
$$Z_2 = 0, \quad C_L^s \equiv 0, \quad s = 1, 2, ..., \tag{20}$$

where $s = 1, 2, ...$ is the iteration number.

4.Presentation of C_L^s as a polynomial $C_L^s = b_0^s + b_1^s Z_2 + b_2^s Z_2^2$, $s = 1, 2, \ldots$.

5. Solution of the problem

$$\frac{dC_G^s}{dZ_1} = -K_G \left[C_G^s - b_0^s - b_1^s (1 - Z_1) - b_2^s (1 - Z_1)^2\right],$$
$$Z_1 = 0, \quad C_G^s = 1. \tag{21}$$

6.Presentation of C_G^s as a polynomial $C_G^s = a_0^s + a_1^s Z_1 + a_2^s Z_1^2$, $s = 1, 2, \ldots$.

The STOP criteria is:

$$\int_0^1 \left(C_G^s - C_G^{(s-1)}\right)^2 dZ_1 \le 10^{-4}. \tag{22}$$

According the industrial conditions the desired absorption degree have to be 94%, i.e. $C_G(1) = 0.06$. The minimization of the least square function

$$F(K_G) = \left[C_G(1) - 0.06\right]^2 \tag{23}$$

permits to be obtained the model parameter $K_G = 3.86$. As a result the model (15)-(18) has the form:

$$\frac{dC_G}{dZ_1} = -3.86\left(C_G - C_L\right); \quad Z_1 = 0, \quad C_G = C_1(1). \tag{24}$$

$$\frac{dC_L}{dZ_2} = 5.32\left(C_G - C_L\right); \quad Z_2 = 0, \quad C_L = 0. \tag{25}$$

$$\frac{dC_1}{dZ} = -K\left(C_1 - C_2\right); \quad Z = 0, \quad C_1 = 1. \tag{26}$$

$$C_2 = \frac{Q_G\left[1 - C_G(1)\right]\chi}{Wk_0\bar{c}_3}. \tag{27}$$

The solution of the model equations (24)-(27) use the next iterative Algorithm II, where as zero iteration step is $C_2^0 = 0.5$:

1. Determination of $C_1^i(Z)$ as a solution of the problem

$$\frac{dC_1^i}{dZ} = -K\left(C_1^i - C_2^{(i-1)}\right); \quad Z = 0, \quad C_1^i = 1; \tag{28}$$

where $i = 1, 2, ...$ is the iteration number.

2. Finding $C_1^i(1)$.

3. Solution of the problem (24), (25), using the algorithm (19)-(22).

4. Finding $C_G(1)$.

5. Calculation of C_2^i, using (27).

6. Checking $\left(C_2^i - C_2^{(i-1)}\right)^2 \le 10^{-4}$?

Yes - continuation of 8.

No - continuation of 7

7.Calculation of $C_0^i = \dfrac{C_2^i + C_2^{(i-1)}}{2}$, laying $C_2^i = C_0^i$, $i = i+1$ and continuation of 1.

8. STOP

4.2. Numerical results

The presented Algorithm I and Algorithm II are used for the solution of the model equations (24)-(27), where $K_g = 3.86$, $K = 1$. As a result is obtained $C_2^{(i_0)} = 0.509$ and concentration distributions, which are presented on the Figs.2-4.

From the model equations solution is obtained the gas outlet (inlet) concentration in the middle (upper) zone of column - $C_G^0 = 0.689$, $C_G(1) = 0.0414p$.

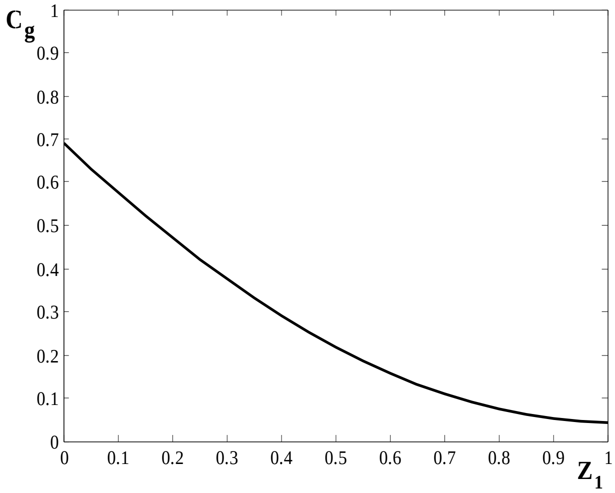

Fig. 2 Evolution of SO_2 concentration in the gas phase $\left(K_g = 3.86,\ K = 1,\ C_2^{(i_0)} = 0.509\right)$

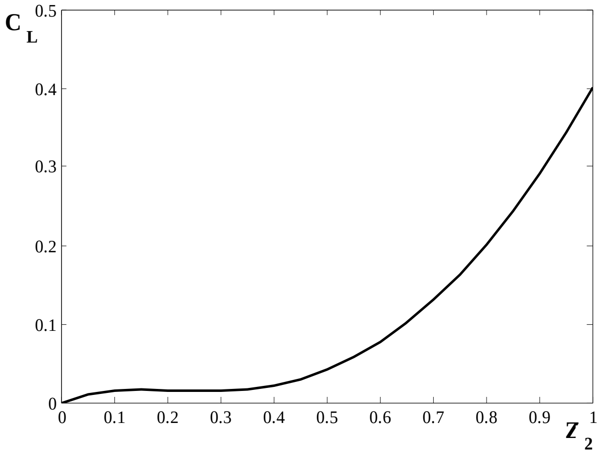

Fig. 3 Evolution of SO_2 concentration in the liquid phase $\left(K_g = 3.86,\ K = 1,\ C_2^{(i_0)} = 0.509\right)$

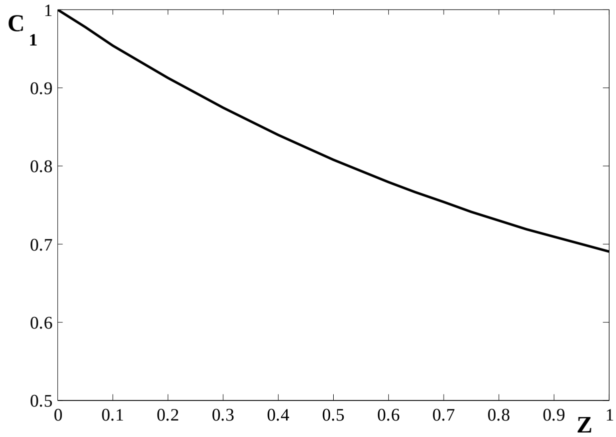

Fig. 4 Evolution of inlet SO_2 concentration in the

gas phase $\left(K_g = 3.86,\ K = 1,\ C_2^{(i_0)} = 0.509\right)$

Considering the desired outlet gas concentration in the column was $C_G\left(Z_1^{(0)}\right) = 0.06a,$, then from the solution of the model equations can be determine the interphase mass transfer coefficient in the upper zone of the column and permits to be obtained required height of the upper part of the column $l_1 = 6.9Z_1^{(0)} = 5.87\ m,\ Z_1^{(0)} = 0.85$ .The increase of the absorber working volume W in the middle zone (2) leads to the decrease of the concentration of SO_2 ($\bar{c}_2$) in the liquid phase (6) and practically C_2 = 0. In these conditions, the height of the upper part of the column (l_1) decrease, if the interphase mass transfer coefficient (K) in the middle zone increase. These results are presented on the Fig. 5.

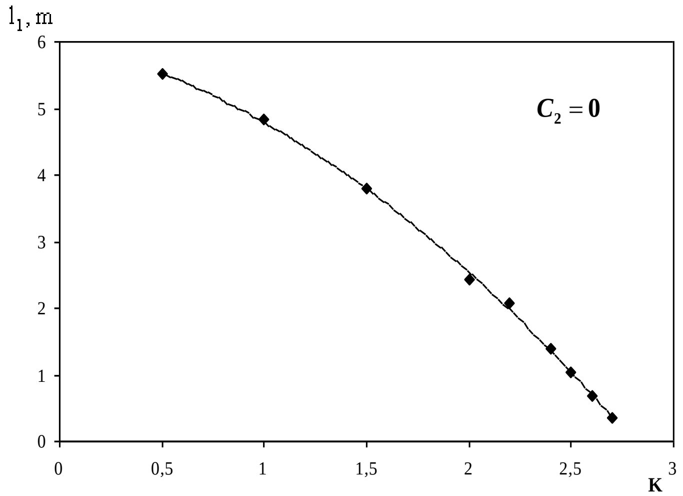

Fig. 5. Height of the upper part of the column (l_1) as function of interphase mass transfer coefficient (K) in the middle zone

Conclusions

The modeling of the gas absorption in a new column apparatus for waste gases purification from SO_2, using two-phase absorbent ($CaCO_3/H_2O$ suspension) is presented. An algorithm for solving a system of model equations is proposed.The distribution of the SO_2 concentration in the two zones of the column is shown and the effect of the mass transfer rate in the middle zone of the column on the total mass transfer rate is demonstrated. The increase of the absorber working volume W in the middle zone of the column leads to the decrease of the inlet concentration of SO_2. In these conditions, the height of the upper part of the column (l_1) decrease. Increasing the intensity of the bubble zone at the bottom of the column (interphase mass transfer coefficient) can result to a significant reduction of the height in the upper part of the apparatus, and thus the entire height of the apparatus.

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