Absorption-adsorption method for waste-free decontamination of gases from SO₂

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In the paper a theoretical approach to model the absorption-adsorption processes for waste-free decontamination of gases from SO₂ is presented. A new method for waste gas purification is realized in two steps: physical absorption of SO₂ with water and chemical adsorption of HSO_3^- from the water solution by synthetic anionite particles. The adsorbent regeneration is made with NH_4OH solution. The obtained $(NH_4)_2SO_3$ (NH_4HSO_3) is used (after reaction with HNO_3) for production of concentrated SO₂ (gas) and NH_4NO_3 (solution). Convection-diffusion and average concentration models of the absorption and adsorption processes are presented.

Keywords: Absorption, adsorption, average concentration model, convection-diffusion model, gas purification, SO₂.

INTRODUCTION

One of the main pollutants in the atmosphere is SO₂. Fossil fuel thermal power plants are considered to be the main source of SO₂ emissions. In industry, the sources are metallurgy, chemical industry and others. In recent years, the increased content of SO₂ in the atmosphere has led to the search for new engineering solutions and cost-effective methods to reduce it. The problem of purification of waste gases from SO₂ focuses the interest of researchers, as its relevance increases over time, changing from technical and economic to environmental.

Different companies (Babcock & Wilcox Power Generation Group, Inc., Alstom Power Italy, Idreco-Insigma-Consortium) propose methods and apparatuses for waste gases purification from SO₂ using a two-phase absorbent ($CaCO_3$ suspension). The adsorption (absorption) of SO₂ on materials derived from natural carbonates [1–3] has the drawback of waste accumulation. The basic problem of the carbonate absorbents is that its chemical reaction with SO₂ leads to CO_2 emission (every molecule of SO₂ absorbed from the air is equivalent to a molecule of CO_2 emitted in the air), because the ecological problems (greenhouse effects) of SO₂ and CO_2 are similar. The large quantity of by-products is a problem, too. Another drawback of these methods is the impossibility for regeneration of the absorbents.

The theoretical analysis [4–10] of the method and apparatus for waste gases purification from SO₂ using a two-phase absorbent ($CaCO_3$ suspension) shows that the process in the absorption column in the gas-liquid drops flow is practically physical absorption as a result of the low concentration of the dissolved $CaCO_3$ and SO₂ in the drops and its brief existence in the gas-liquid dispersion. An increase of the process efficiency is proposed in the patent [11], where an absorption column with two absorption zones (lower liquid-gas bubbles zone and upper gas-liquid drops zone) is used. This creates a possibility to increase the absorption degree or to lower the column height. Many developments are dedicated to improving the design of the apparatuses for obtaining products and quality control to expand their application [12-15].

The difficulties in the purification of SO₂ gases in the energy sector stem from its low concentration (0.1 - 0.5% vol.) and high waste gas flows. One of the possibilities for their solution is the use of regenerable sorbents. The use of synthetic anionites (basic anion-exchange resins - R-OH form of Amberlite, Duolite, Kastel, Varion, Wofatit) as adsorbents [16–18] for gas purification from SO₂ provides possibilities for adsorbent regeneration. The chemical reaction of SO₂ with the synthetic anionites can be presented by the stoichiometric equation: $SO_2 + R-OH \rightarrow R-HSO_3$.

After saturation of the synthetic anionite particles with sulfur dioxide, the adsorbent regeneration can be carried out with a water solution of NH_4OH:

$$R-HSO_3 + 2NH_4OH \rightarrow R-OH + (NH_4)_2SO_3 \quad (1)$$
$$(or\ NH_4HSO_3).$$
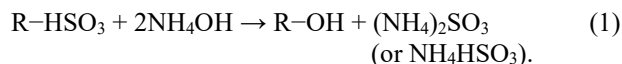
In the presented method [19] the adsorption is realized in the gas phase, while the adsorbent regeneration is realized in the liquid phase.

In this scientific research, a theoretical absorption-adsorption approach is proposed to solve the problem of waste gases purification from SO₂.

Absorption-adsorption approach

The main disadvantages of the $CaCO_3$ suspension method – CO_2 emission, gypsum accumulation and

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inability to regenerate the adsorbent – are handled by the patent [19] (see Fig. 1), where the waste gas purification is realized in two steps – physical absorption of SO_2 with water:

$$H_2O + SO_2 \rightarrow HSO_3^- + H^+. \qquad (2)$$

and chemical adsorption of HSO_3^- from the water solution by synthetic anionite particles:

$$HSO_3^- + H^+ + R\text{-}OH \rightarrow R\text{-}HSO_3 + H_2O. \qquad (3)$$

The adsorbent regeneration is made with NH_4OH solution (see (1)). The obtained $(NH_4)_2SO_3$ (NH_4HSO_3) is used (after reaction with HNO_3) for production of concentrated SO_2 (gas) and NH_4NO_3 (solution).

In Fig. 1 the gas enters the middle part of the column 2 through the inlet 1, gets in contact with the absorbent (H_2O) in the upper part of the column, where a gas-liquid drops counter-current flow is formed, passes through the liquid drops separator 4 and out through the outlet 5. The absorbent enters the column through the inlets 11 and spreader 3, absorbs the SO_2 from the gas in the middle part of the column, collects at the bottom of the column and

goes out through the exit 6. After that the absorbent ($H_2O + SO_2$) passes through one of the valves 7 and enters one of the adsorbers 8, where SO_2 is adsorbed on the particles of synthetic anionite and the regenerated absorbent (H_2O) is returned by pumps 9 and valves 10 to the absorption column through the inlets 11. The absorbent, separated in the separator 4, passes through the outlets 12 and valve 13 and enters the adsorbers 8. After the synthetic anionite particles have been saturated with sulfur dioxide in the adsorbers 8 the adsorbent regeneration is realized by means of a water solution of NH_4OH, which is obtained in the NH_3 absorber 14 and through the pump 15 and the valves 16 enters the adsorbers 8. The water solution of $(NH_4)_2SO_3$ obtained in 8 (after adsorbent regeneration) enters through the pumps 9 and valves 17 in the reactor 18, where it reacts with HNO_3 (coming from the tank 19). The obtained concentrated SO_2 (gas) and NH_4NO_3 solution goes out of the system through the outlet 21. The pump 20 allows the solution of $(NH_4)_2SO_3$ to be re-circulated in order to achieve higher concentration.

Fig. 1. Column apparatus for absorption-adsorption waste-free decontamination of gases from SO_2

(1, 11-inlets; 2-column; 3-spreader; 4-separator; 5, 12, 21-outlets; 6-exit; 7, 10, 13, 16, 17-valves; 8-adsorbers; 9, 15, 20-pumps; 14-absorber; 18-reactor; 19-tank)

The main processes in the absorption-adsorption method are the physical absorption of SO_2 by H_2O in a counter-current gas-liquid drops system and a chemical adsorption of SO_2 by synthetic anionite particles in a liquid-solid system.

Absorption-adsorption modeling

The modeling of a non-stationary (as a result of the adsorbent saturation) absorption-adsorption cycle of the method for gas purification from SO_2 uses a combination of the physical absorption and chemical adsorption models [20]:

$$\frac{\partial c_1}{\partial t}+u_1\frac{\partial c_1}{\partial z_1}=D_1\left(\frac{\partial^2 c_1}{\partial z_1^2}+\frac{1}{r_1}\frac{\partial c_1}{\partial r_1}+\frac{\partial^2 c_1}{\partial r_1^2}\right)-k_0\left(c_1-\chi c_2\right);$$

$$\frac{\partial c_2}{\partial t}+u_2\frac{\partial c_2}{\partial z_2}=D_2\left(\frac{\partial^2 c_2}{\partial z_2^2}+\frac{1}{r_1}\frac{\partial c_2}{\partial r_1}+\frac{\partial^2 c_2}{\partial r_1^2}\right)+k_0\left(c_1-\chi c_2\right);$$

$$t=0,\quad c_1\equiv c_1^0,\quad c_2\equiv 0;$$

$$r_1=0,\quad \frac{\partial c_1}{\partial r_1}=\frac{\partial c_2}{\partial r_1}\equiv 0;\quad r_1=r_{10},\quad \frac{\partial c_1}{\partial r_1}=\frac{\partial c_2}{\partial r_1}\equiv 0; \tag{4}$$

$$z_1=0,\quad c_1\left(r_1,0\right)\equiv c_1^0,\quad u_1^0 c_1^0\equiv u_1\left(r_1\right)c_1^0-D_1\left(\frac{\partial c_1}{\partial z_1}\right)_{z_1=0};$$

$$z_2=0,\quad c_2\left(r_1,0\right)\equiv \overline{c}_{12}\left(l_2\right),$$

$$u_2^0\overline{c}_{12}\left(l_2\right)\equiv u_2\left(r_1\right)\overline{c}_{12}\left(l_2\right)-D_2\left(\frac{\partial c_2}{\partial z_2}\right)_{z_2=0}.$$

$$\frac{\partial c_{12}}{\partial t}+u\frac{\partial c_{12}}{\partial z}=D_{12}\left(\frac{\partial^2 c_{12}}{\partial z^2}+\frac{1}{r}\frac{\partial c_{12}}{\partial r_2}+\frac{\partial^2 c_{12}}{\partial r_2^2}\right)-k_1\left(c_{12}-c_{13}\right);$$

$$\frac{dc_{13}}{dt}=k_1\left(c_{12}-c_{13}\right)-kc_{13}c_{23}=0;\quad \frac{dc_{23}}{dt}=-kc_{13}c_{23};$$

$$t=0,\quad c_{12}\equiv 0,\quad c_{13}\equiv 0,\quad c_{23}\equiv c_{23}^0; \tag{5}$$

$$r_2=0,\quad \frac{\partial c_{12}}{\partial r_2}\equiv 0;\quad r_2=r_{20},\quad \frac{\partial c_{12}}{\partial r_2}\equiv 0;$$

$$z=0,\quad c_{12}\left(r_2,0\right)\equiv \overline{c}_2\left(l_1\right),$$

$$u^0\overline{c}_2\left(l_1\right)\equiv u\left(r_2\right)\overline{c}_2\left(l_1\right)-D_2\left(\frac{\partial c_{12}}{\partial z}\right)_{z=0}.$$

In the absorber model (4) c_1, c_2, D_1, D_2 are the concentrations and diffusivities of SO_2 in the gas and liquid phases, u_1, u_2 − the velocities in the gas and liquid phases, r_1, l_1 − the radius and height of the working zone of the column, t − the time. In the adsorber model (5) c_{12}, D_{12} are the concentration and diffusivity of SO_2 in the liquid phase in the adsorber, c_{13}, c_{23} − the concentrations of SO_2 and active sides in the adsorbent, u − the velocity in the liquid phases, r_2, l_2 − the radius and height of the working zone of the column, t − the time. In the absorption-adsorption cycle the average outlet concentration of

SO_2 in the liquid phase of the absorber is the inlet concentration of SO_2 in the liquid phase of the adsorber ($c_{12}\left(r_2,0\right)\equiv \overline{c}_2\left(l_1\right)$), while the average outlet concentration of SO_2 in the liquid phase of the adsorber is the inlet concentration of SO_2 in the liquid phase of the absorber ($c_2\left(r_1,0\right)\equiv \overline{c}_{12}\left(l_2\right)$).

Generalized analysis

The use of dimensionless (generalized) variables [20-22] allows to make a qualitative analysis of the models (4, 5), whereas characteristic scales are used for the average velocity, the inlet and initial concentrations, the characteristic time t_0 (saturation time of the adsorbent) and the column's dimensions (r_1, r_2, l_1, l_2):

$$T=\frac{t}{t_0},\quad R_1=\frac{r_1}{r_{10}},\quad R_2=\frac{r_2}{r_{20}},$$

$$Z=\frac{z}{l_2},\quad Z_1=\frac{z_1}{l_1},\quad Z_2=\frac{z_2}{l_1},$$

$$U=\frac{u}{u^0},\quad U_1=\frac{u_1}{u_1^0},\quad U_2=\frac{u_2}{u_2^0},\quad C_1=\frac{c_1}{c_1^0},\quad C_2=\frac{c_2\chi}{c_1^0}, \tag{6}$$

$$C_{12}=\frac{c_{12}\chi}{c_1^0},\quad C_{13}=\frac{c_{13}\chi}{c_1^0},\quad C_{23}=\frac{c_{23}}{c_{23}^0}.$$

When (6) is put into (4) and (5), the models in generalized variables take the form:

$$\gamma_1\frac{\partial C_1}{\partial T}+U_1\frac{\partial C_1}{\partial Z_1}=$$

$$=Fo_1\left(\beta_1\frac{\partial^2 C_1}{\partial Z_1^2}+\frac{1}{R_1}\frac{\partial C_1}{\partial R_1}+\frac{\partial^2 C_1}{\partial R_1^2}\right)-K_1\left(C_1-C_2\right);$$

$$\gamma_2\frac{\partial C_2}{\partial T}+U_2\frac{\partial C_2}{\partial Z_2}=$$

$$=Fo_2\left(\beta_1\frac{\partial^2 C_2}{\partial Z_2^2}+\frac{1}{R_1}\frac{\partial C_2}{\partial R_1}+\frac{\partial^2 C_2}{\partial R_1^2}\right)+K_2\left(C_1-C_2\right);$$

$$T=0,\quad C_1\equiv 1,\quad C_2\equiv 0;$$

$$R_1=0,\quad \frac{\partial C_1}{\partial R_1}=\frac{\partial C_2}{\partial R_1}\equiv 0;$$

$$R_1=1,\quad \frac{\partial C_1}{\partial R_1}=\frac{\partial C_2}{\partial R_1}\equiv 0;$$

$$Z_1=0,\quad C_1\left(R_1,0\right)\equiv 1,\quad 1\equiv U_1\left(R_1\right)-Pe_1^{-1}\left(\frac{\partial C_1}{\partial Z_1}\right)_{Z_1=0};$$

$$Z_2=0,\quad C_2\left(R_1,0\right)\equiv \overline{C}_{12}\left(1\right), \tag{7}$$

$$1\equiv U_2\left(R_1\right)-\frac{Pe_2^{-1}}{\overline{C}_{12}\left(1\right)}D_2\left(\frac{\partial C_2}{\partial Z_2}\right)_{Z_2=0}.$$

$$\gamma_0 \frac{\partial C_{12}}{\partial T} + U \frac{\partial C_{12}}{\partial Z} =$$

$$= \mathrm{Fo}_0 \left(\beta_0 \frac{\partial^2 C_{12}}{\partial Z^2} + \frac{1}{R_2} \frac{\partial C_{12}}{\partial R_2} + \frac{\partial^2 C_{12}}{\partial R_2^2} \right) - K_0 \left(C_{12} - C_{13} \right);$$

$$\frac{dC_{13}}{dT} = K_3 \left(C_{12} - C_{13} \right) - K_4 C_{13} C_{23} = 0;$$

$$\frac{dC_{23}}{dT} = -K_5 C_{13} C_{23}; \qquad (8)$$

$$T = 0, \quad C_{12} \equiv 0, \quad C_{13} \equiv 0, \quad C_{23} \equiv 1;$$

$$R_2 = 0, \quad \frac{\partial C_{12}}{\partial R_2} \equiv 0; \quad R_2 = 1, \quad \frac{\partial C_{12}}{\partial R_2} \equiv 0;$$

$$Z = 0, \quad C_{12}\left(R_2, 0 \right) \equiv \bar{C}_2 \left(1 \right),$$

$$1 \equiv U\left(R_2 \right) - \frac{\mathrm{Pe}_0^{-1}}{\bar{C}_2 \left(1 \right)} \left(\frac{\partial C_{12}}{\partial Z} \right)_{Z=0}.$$

The following parameters are used in (7), (8):

$$K_0 = \frac{k_1 l_2}{u^0}, \quad K_1 = \frac{k_0 l_1}{u_1^0}, \quad K_2 = \frac{k_0 l_1 \chi}{u_2^0}, \quad K_3 = k_1 t_0,$$

$$K_4 = k t_0 c_{23}^0, \quad K_5 = k t_0 \frac{c_1^0}{\chi}, \quad \beta_0 = \frac{r_{20}^2}{l_2^2}, \quad \beta_1 = \frac{r_{10}^2}{l_1^2},$$

$$\gamma_0 = \frac{l_2}{t_0 u^0}, \quad \gamma_1 = \frac{l_1}{t_0 u_1^0}, \quad \gamma_2 = \frac{l_1}{t_0 u_2^0}, \qquad (9)$$

$$\mathrm{Fo}_0 = \frac{D_2 l_2}{u^0 r_{20}^2}, \quad \mathrm{Fo}_1 = \frac{D_1 l_1}{u_1^0 r_{10}^2}, \quad \mathrm{Fo}_1 = \frac{D_2 l_1}{u_2^0 r_{10}^2},$$

$$\bar{C}_2 \left(1 \right) = 2 \int_0^1 R_1 C_2 \left(R_1, 1 \right) dR_1, \quad \bar{C}_{12} \left(1 \right) = 2 \int_0^1 R_2 C_{12} \left(R_2, 1 \right) dR_2.$$

For lengthy processes $(0 = \gamma_0 \sim \gamma_1 \sim \gamma_2 \le 10^{-2})$, high columns $(0 = \beta_0 \sim \beta_1 \le 10^{-2})$ and typical fluid velocities $(0 = \mathrm{Fo}_0 \sim \mathrm{Fo}_1 \sim \mathrm{Fo}_2 \le 10^{-2})$ the model has the form:

$$U_1 \frac{dC_1}{dZ_1} = -K_1 \left(C_1 - C_2 \right); \quad Z_1 = 0, \quad C_1 \left(R_1, 0 \right) \equiv 1; \qquad (10)$$

$$U_2 \frac{dC_2}{dZ_2} = K_2 \left(C_1 - C_2 \right); \quad Z_2 = 0, \quad C_2 \left(R_1, 0 \right) \equiv \bar{C}_{12} \left(1 \right).$$

$$U \frac{dC_{12}}{dZ} = -K_0 \left(C_{12} - C_{13} \right);$$

$$\frac{dC_{13}}{dT} = K_3 \left(C_{12} - C_{13} \right) - K_4 C_{13} C_{23} = 0;$$

$$\frac{dC_{23}}{dT} = -K_5 C_{13} C_{23}; \qquad (11)$$

$$Z = 0, \quad C_{12} \left(R_2, 0 \right) \equiv \bar{C}_2 \left(1 \right);$$

$$T = 0, \quad C_{13} \equiv 0, \quad C_{23} \equiv 1.$$

Average-concentration model

The presented models (10, 11) show that in the practical cases convective type of models have to be used:

$$u_1 \frac{dc_1}{dz_1} = -k_0 \left(c_1 - \chi c_2 \right); \quad z_1 = 0, \quad c_1 \left(t, r_1, 0 \right) \equiv c_1^0;$$

$$u_2 \frac{dc_2}{dz_2} = k_0 \left(c_1 - \chi c_2 \right); \quad z_2 = 0, \quad c_2 \left(t, r_1, 0 \right) \equiv \bar{c}_{12} \left(t, l_2 \right). \qquad (12)$$

$$u \frac{dc_{12}}{dz} = -k_1 \left(c_{12} - c_{13} \right);$$

$$\frac{dc_{13}}{dt} = k_1 \left(c_{12} - c_{13} \right) - k c_{13} c_{23} = 0;$$

$$\frac{dc_{23}}{dt} = -k c_{13} c_{23}; \qquad (13)$$

$$z = 0, \quad c_{12} \left(t, r_2, 0 \right) \equiv \bar{c}_2 \left(t, l_1 \right);$$

$$t = 0, \quad c_{13} \left(0, r_2, z \right) \equiv 0, \quad c_{23} \left(0, r_2, z \right) \equiv c_{23}^0.$$

The average values of the velocities and concentrations in the column's cross-sectional area can be obtained [20-22] using the expressions:

$$\bar{u} = \frac{2}{r_{20}^2} \int_0^{r_{20}} r_2 u \left(r_2 \right) dr_2 = u^0,$$

$$\bar{u}_1 = \frac{2}{r_{10}^2} \int_0^{r_{10}} r_1 u_1 \left(r_1 \right) dr_1 = u_1^0,$$

$$\bar{u}_2 = \frac{2}{r_{10}^2} \int_0^{r_{10}} r_1 u_2 \left(r_1 \right) dr_1 = u_2^0,$$

$$\bar{c}_1 \left(t, z_1 \right) = \frac{2}{r_{10}^2} \int_0^{r_{10}} r_1 c_1 \left(t, r_1, z_1 \right) dr_1,$$

$$\bar{c}_2 \left(t, z_2 \right) = \frac{2}{r_{10}^2} \int_0^{r_{10}} r_1 c_2 \left(t, r_1, z_2 \right) dr_1,$$

$$\bar{c}_{12} \left(t, z \right) = \frac{2}{r_{20}^2} \int_0^{r_{20}} r_2 c_{12} \left(t, r_2, z \right) dr_2,$$

$$\bar{c}_{13} \left(t, z \right) = \frac{2}{r_{20}^2} \int_0^{r_{20}} r_2 c_{13} \left(t, r_2, z \right) dr_2,$$

$$\bar{c}_{23} \left(t, z \right) = \frac{2}{r_{20}^2} \int_0^{r_{20}} r_2 c_{23} \left(t, r_2, z \right) dr_2. \qquad (14)$$

The velocities and concentration distributions in (12) and (13) can be presented with the help of the average functions (14):

$$u\left(r_2 \right) = \bar{u} \tilde{u} \left(r_2 \right), u_1 \left(r_1 \right) = \bar{u}_1 \tilde{u}_1 \left(r_1 \right),$$

$$u_2 \left(r_1 \right) = \bar{u}_2 \tilde{u}_2 \left(r_1 \right),$$

$$c_1 \left(t, r_1, z_1 \right) = \bar{c}_1 \left(t, z_1 \right) \tilde{c}_1 \left(t, r_1, z_1 \right),$$

$$c_2 \left(t, r_1, z_2 \right) = \bar{c}_2 \left(t, z_2 \right) \tilde{c}_1 \left(t, r_1, z_2 \right), \qquad (15)$$

$$c_{12} \left(t, r_2, z \right) = \bar{c}_{12} \left(t, z \right) \tilde{c}_{12} \left(t, r_2, z \right),$$

$$c_{13} \left(t, r_2, z \right) = \bar{c}_{13} \left(t, z \right) \tilde{c}_{13} \left(t, r_2, z \right),$$

$$c_{23} \left(t, r_2, z \right) = \bar{c}_{23} \left(t, z \right) \tilde{c}_{23} \left(t, r_2, z \right).$$

Here $\tilde{u}(r_2)$, $\tilde{u}_1(r_1)$, $\tilde{u}_2(r_1)$, $\tilde{c}_1(t,r_1,z_1)$,
$\tilde{c}_2(t,r_1,z_2)$, $\tilde{c}_{12}(t,r_2,z)$, $\tilde{c}_{13}(t,r_2,z)$, $\tilde{c}_{23}(t,r_2,z)$ present the radial non-uniformity of the velocity and the concentration distributions satisfying the conditions:

$$\frac{2}{r_{20}^2}\int_0^{r_{20}} r_2\tilde{u}(r_2)\,dr_2 = 1, \quad \frac{2}{r_{10}^2}\int_0^{r_{10}} r_1\tilde{u}_1(r_1)\,dr_1 = 1,$$

$$\frac{2}{r_{10}^2}\int_0^{r_{10}} r_1\tilde{u}_2(r_1)\,dr_1 = 1, \quad \int_0^{r_{10}} r_1\tilde{c}_1(t,r_1,z_1)\,dr_1 = 1,$$

$$\frac{2}{r_{10}^2}\int_0^{r_{10}} r_1\tilde{c}_2(t,r_1,z_2)\,dr_1 = 1, \quad \frac{2}{r_{20}^2}\int_0^{r_{20}} r_2\tilde{c}_{12}(t,r_2,z)\,dr_2 = 1, \tag{16}$$

$$\frac{2}{r_{20}^2}\int_0^{r_{20}} r_2\tilde{c}_{13}(t,r_2,z)\,dr_2 = 1, \quad \frac{2}{r_{20}^2}\int_0^{r_{20}} r_2\tilde{c}_{23}(t,r_2,z)\,dr_2 = 1.$$

The use of the averaging procedure [20] leads to:

$$\alpha_1\bar{u}_1\frac{d\bar{c}_1}{dz_1} + \frac{d\alpha_1}{dz_1}\bar{u}_1\bar{c}_1 = -k_0(\bar{c}_1 - \chi\bar{c}_2);$$

$$\alpha_2\bar{u}_2\frac{d\bar{c}_2}{dz_2} + \frac{d\alpha_2}{dz_2}\bar{u}_2\bar{c}_2 = k_0(\bar{c}_1 - \chi\bar{c}_2); \tag{17}$$

$$z_1 = 0, \quad \bar{c}_1(t,0) \equiv c_1^0;$$

$$z_2 = 0, \quad \bar{c}_2(t,0) \equiv \bar{c}_{12}(t,l_2).$$

$$\alpha\bar{u}\frac{d\bar{c}_{12}}{dz} + \frac{d\alpha}{dz}\bar{u}\,\bar{c}_{12} = -k_1(\bar{c}_{12} - \bar{c}_{13});$$

$$\frac{d\bar{c}_{13}}{dt} = k_1(\bar{c}_{12} - \bar{c}_{13}) - \beta k\bar{c}_{13}\bar{c}_{23} = 0;$$

$$\frac{d\bar{c}_{23}}{dt} = -\beta k\,\bar{c}_{13}\bar{c}_{23}; \tag{18}$$

$$z = 0, \quad \bar{c}_{12}(t,0) \equiv \bar{c}_2(t,l_1);$$

$$t = 0, \quad \bar{c}_{13}(0,z) \equiv 0, \quad \bar{c}_{23}(0,z) \equiv c_{23}^0.$$

The following functions are used in (17) and (18):

$$\alpha(t,z) = \frac{2}{r_{20}^2}\int_0^{r_{20}} r_2\tilde{u}(r_2)\tilde{c}_{12}(t,r_2,z)\,dr_2,$$

$$\alpha_1(t,z_1) = \frac{2}{r_{10}^2}\int_0^{r_{10}} r_1\tilde{u}_1(r_1)\tilde{c}_1(t,r_1,z_1)\,dr_1,$$

$$\alpha_2(t,z_2) = \frac{2}{r_{10}^2}\int_0^{r_{10}} r_1\tilde{u}_2(r_1)\tilde{c}_2(t,r_1,z_2)\,dr_1, \tag{19}$$

$$\beta(t,z) = \frac{2}{r_{20}^2}\int_0^{r_{20}} r_2\tilde{c}_{13}(t,r_2,z)\tilde{c}_{23}(t,r_2,z)\,dr_2.$$

Generalized analysis

The use of the dimensionless (generalized) variables

$$T = \frac{t}{t_0}, \quad Z = \frac{z}{l_2},$$

$$Z_1 = \frac{z_1}{l_1}, \quad Z_2 = \frac{z_2}{l_1},$$

$$\bar{C}_1 = \frac{\bar{c}_1}{c_1^0}, \quad \bar{C}_2 = \frac{\bar{c}_2\chi}{c_1^0}, \tag{20}$$

$$\bar{C}_{12} = \frac{\bar{c}_{12}\chi}{c_1^0}, \quad \bar{C}_{13} = \frac{\bar{c}_{13}\chi}{c_1^0}, \quad \bar{C}_{23} = \frac{\bar{c}_{23}}{c_{23}^0}.$$

leads to:

$$A_1\frac{d\bar{C}_1}{dZ_1} + \frac{dA_1}{dZ_1}\bar{C}_1 = -K_1(\bar{C}_1 - \bar{C}_2);$$

$$A_2\frac{d\bar{C}_2}{dZ_2} + \frac{dA_2}{dZ_2}\bar{C}_2 = K_2(\bar{C}_1 - \bar{C}_2); \tag{21}$$

$$Z_1 = 0, \quad \bar{C}_1(T,0) \equiv 1;$$

$$Z_2 = 0, \quad \bar{C}_2(T,0) \equiv \bar{C}_{12}(T,1).$$

$$A\frac{d\bar{C}_{12}}{dZ} + \frac{dA}{dZ}\bar{C}_{12} = -K_0(\bar{C}_{12} - \bar{C}_{13});$$

$$\frac{d\bar{C}_{13}}{dT} = K_3(\bar{C}_{12} - \bar{C}_{13}) - BK_4\bar{C}_{13}\bar{C}_{23} = 0;$$

$$\frac{d\bar{C}_{23}}{dT} = -BK_5\bar{C}_{13}\bar{C}_{23}; \tag{22}$$

$$Z = 0, \quad \bar{C}_{12}(T,0) \equiv \bar{C}_2(T,1);$$

$$T = 0, \quad \bar{C}_{13}(0,Z) \equiv 0, \quad \bar{C}_{23}(0,Z) \equiv 1.$$

The following functions are used in (21) and (22):

$$\bar{C}_1(T,Z_1) = 2\int_0^1 R_1 C_1(T,R_1,Z_1)\,dR_1,$$

$$\bar{C}_2(T,Z_2) = 2\int_0^1 R_1 C_2(T,R_1,Z_2)\,dR_1,$$

$$\bar{C}_{13}(T,Z) = 2\int_0^1 R_2 C_{13}(T,R_2,Z)\,dR_2,$$

$$\bar{C}_{23}(T,Z) = 2\int_0^1 R_2 C_{23}(T,R_2,Z)\,dR_2.$$

$$A(T,Z) = \alpha(t_0T,l_2Z) = \alpha(t,z) =$$
$$= 2\int_0^1 RU(R_2)\frac{C_{12}(T,R_2,Z)}{\bar{C}_{12}(T,Z)}\,dR_2$$

$$A_1(T,Z_1) = \alpha_1(t_0T,l_1Z_1) = \alpha_1(t,z_1) =$$
$$= 2\int_0^1 R_1 U_1(R_1)\frac{C_1(T,R_1,Z_1)}{\bar{C}_1(T,Z_1)}\,dR_1$$

$$A_2(T,Z_2) = \alpha_2(t_0 T, l_1 Z_2) = \alpha_2(t,z_2) =$$
$$= 2\int_0^1 R_1 U_2(R_1)\frac{C_2(T,R_1,Z_2)}{\bar{C}_2(T,Z_2)}dR_1$$
$$B(T,Z) = \beta(t_0 T, l_2 Z) = \beta(t,z) =$$
$$= 2\int_0^1 R_2 \frac{C_{13}(T,R_2,Z)}{\bar{C}_{13}(T,Z)}\frac{C_{23}(T,R_2,Z)}{\bar{C}_{23}(T,Z)}dR_2 \qquad (23)$$

In [20] it was shown that $B(T,Z) \equiv 1$ and $A(T,Z), A_1(T,Z_1), A_2(T,Z_2)$ can be presented as linear approximations:

$$A = 1 + a_z Z + a_t T,$$
$$A_1 = 1 + a_z^1 Z_1 + a_t^1 T, \qquad (24)$$
$$A_2 = 1 + a_z^2 Z_2 + a_t^2 T.$$

As a result, the model of the absorption-desorption process has the form:

$$\left(1 + a_z^1 Z_1 + a_t^1 T\right)\frac{d\bar{C}_1}{dZ_1} + a_z^1 \bar{C}_1 = -K_1\left(\bar{C}_1 - \bar{C}_2\right);$$
$$\left(1 + a_z^2 Z_2 + a_t^2 T\right)\frac{d\bar{C}_2}{dZ_2} + a_z^2 \bar{C}_2 = K_2\left(\bar{C}_1 - \bar{C}_2\right); \qquad (25)$$
$$Z_1 = 0, \quad \bar{C}_1(T,0) \equiv 1; \quad Z_2 = 0, \quad \bar{C}_2(T,0) \equiv \bar{C}_{12}(T,1).$$

$$\left(1 + a_z Z + a_t T\right)\frac{d\bar{C}_{12}}{dZ} + a_z \bar{C}_{12} = -K_0\left(\bar{C}_{12} - \bar{C}_{13}\right);$$
$$\frac{d\bar{C}_{13}}{dT} = K_3\left(\bar{C}_{12} - \bar{C}_{13}\right) - K_4 \bar{C}_{13}\bar{C}_{23} = 0;$$
$$\frac{d\bar{C}_{23}}{dT} = -K_5 \bar{C}_{13}\bar{C}_{23}; \qquad (26)$$
$$Z = 0, \quad \bar{C}_{12}(T,0) \equiv \bar{C}_2(T,1);$$
$$T = 0, \quad \bar{C}_{13}(0,Z) \equiv 0, \quad \bar{C}_{23}(0,Z) \equiv 1.$$

Algorithm of the solution

The solution of (25) and (26) can be obtained as five matrix forms:

$$\bar{C}_1(T,Z) = \left\|C_{(1)\tau\zeta}\right\|, \quad \bar{C}_2(T,Z) = \left\|C_{(2)\tau\zeta}\right\|,$$
$$\bar{C}_{12}(T,Z) = \left\|C_{(12)\tau\zeta}\right\|, \quad \bar{C}_{13}(T,Z) = \left\|C_{(13)\tau\zeta}\right\|,$$
$$\bar{C}_{23}(T,Z) = \left\|C_{(23)\tau\zeta}\right\|; \qquad (27)$$
$$0 \le T \le 1, \quad T = \frac{\tau - 1}{\tau^0 - 1}, \quad \tau = 1,2,...,\tau^0;$$
$$0 \le Z \le 1, \quad Z = \frac{\zeta - 1}{\zeta^0 - 1}, \quad \zeta = 1,2,...,\zeta^0; \quad \tau^0 = \zeta^0.$$

A multi-step approach may be used. At each step the problems (25) and (26) have to be solved consecutively, where T is a parameter in (25), Z is a parameter in (26), $\bar{C}_2^{(s)}(T,0) \equiv \bar{C}_{12}^{(s-1)}(T,1), \bar{C}_{12}^{(0)}(T,1) \equiv 0$,

where the superscript values $(s = 0,1,2,...)$ are the step numbers.

Parameters identification

The availability of experimental data for the SO₂ concentrations in the gas and liquid phases at the absorber and adsorber outlets ($\bar{C}_1^{\exp}(T_n,1), \bar{C}_{12}^{\exp}(T_n,1), T_n = 0.05n, n = 1,2,...,20$) permits to use the following algorithm for the parameters identification in the model (25), (26):

1. Put $a_z = a_t = a_z^1 = a_t^1 = a_z^2 = a_t^2 = 0$ in (25), (26) and minimize the least squares functions:

$$F_1(K_1,K_2) = \sum_{n=1}^{20}\left[\bar{C}_1(T_n,1) - \bar{C}_1^{\exp}(T_n,1)\right]^2,$$
$$F_2(K_0,K_3,K_4,K_5) = \sum_{n=1}^{20}\left[\bar{C}_{12}(T_n,1) - \bar{C}_{12}^{\exp}(T_n,1)\right]^2, \qquad (28)$$

where $\bar{C}_1(T_n,1), \bar{C}_{12}(T_n,1)$ are obtained as a solution of (25), (26) for $T_n = 0.05n, n = 1,2,...,20$.

2. Enter the obtained parameter values ($K_p, p = 0,1,...,5$) in (25), (26) and minimize the least squares functions:

$$F_3(a_z^1,a_t^1,a_z^2,a_t^2) = \sum_{n=1}^{20}\left[\bar{C}_1(T_n,1) - \bar{C}_1^{\exp}(T_n,1)\right]^2,$$
$$F_4(a_z,a_t) = \sum_{n=1}^{20}\left[\bar{C}_{12}(T_n,1) - \bar{C}_{12}^{\exp}(T_n,1)\right]^2, \qquad (29)$$

where $\bar{C}_1(T_n,1), \bar{C}_{12}(T_n,1)$ are obtained as a solution of (25), (26) for $T_n = 0.05n, n = 1,2,...,20$.

3. Enter the calculated values of the parameters $a_z,a_t,a_z^1,a_t^1,a_z^2,a_t^2$ in (25), (26) and minimize the least squares functions (29), etc.

CONCLUSION

The emphasis of the presented research is on eco-technologies and waste-free production. The proposed patent [19] makes it possible to create a waste-free technology for waste gases purification from SO₂ by means of regenerable absorbent and adsorbent. Convection-diffusion and average concentration models of the absorption and adsorption processes permit to model the patent processes.

The new technology will help to solve the problems faced by entrepreneurs in implementing innovations and compliance with environmental standards. Obtaining valuable products according to the proposed technology will allow for cost-effective purification of SO₂ gases.

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