ON THE SO$_2$ PROBLEM OF SOLID FUEL COMBUSTION

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Introduction

The thermal power plants, which use sulfur-rich fuels, pose the problem of sulfur dioxide removal from the waste gases. This problem is complicated by the fact, that it is required to purify huge amounts of gas with low SO$_2$ concentration [1–3].

The huge gas amounts need big apparatuses size, which is possible to be decreased if the absorption rate is maximal. This rate is proportional to the concentration difference $\tilde{c}_0 - \tilde{c}^*$, where $\tilde{c}_0$ (kgmol.m^{-3}) is SO$_2$ concentration in the gas volume and $\tilde{c}^*$ (kgmol.m^{-3}) is SO$_2$ concentration in the gas phase at the gas-liquid interphase [4, 5]. A maximal absorption rate is possible if $\tilde{c}^* = 0$, i.e. in the cases of very fast irreversible chemical reactions of SO$_2$ in liquid phase, i.e., the using of highly concentrated alkaline absorbents.

The SO$_2$ purification of huge amounts of waste gases from the thermal power plants needs inexpensive absorbent (CaCO$_3$ suspensions). The presence of the active component in the absorbent as a solution and solid phase leads to an increasing of the absorption capacity of the absorbent, but the introduction of a new process (the dissolution of the solid phase) creates conditions for variations of the absorption mechanism (interphase mass transfer through two interphase surfaces – gas/liquid and liquid/solid).

1. Diffusion type of model

The using of alkaline absorbents (for example water solutions of Na$_2$CO$_3$) is not effective from an economic perspective, because of the high prices and large quantity of by-products. The two-phases absorbent [7-9] (as water suspensions of CaCO$_3$) have a low price and a big absorption capacity.

Many companies provide methods and apparatuses for waste gases purification from SO$_2$, using two-phases absorbent. The gas enters in the middle of the counter-current column, contacts with the absorbent drops and exits from the top. The collected absorbent in the bottom half of the column returns through the top of the column. A theoretical analysis of this gas absorption with two-phases absorbent (CaCO$_3$/H$_2$O suspension) will be presented.

The gas absorption process practically is realized in gas-liquid dispersion, moving in column apparatuses, where the dispersed phase is liquid drops. In these hydrodynamic conditions the velocity distributions in the gas and liquid phases in the column are not possible to be obtained and a qualitative theoretical analysis of the absorption kinetics, using the diffusion type of model [6, 10], is possible to be made only.

Let's consider a moving gas-liquid dispersion in column apparatus, where a SO_2 absorption with two-phases absorbent is realized. The mathematical model of the gas absorption process will be created in the approximations of the mechanics of continua [6], where the mathematical point is equivalent to the medium elementary volume, which is sufficiently small with respect to the column volume and at the same time sufficiently large with respect to the intermolecular distances in the medium.

The base of the model will be the convection-diffusion equation [6, 10]. The convective transfer in the elementary volume results from laminar or turbulent (large-scale pulsations) flows. The diffusive transfer is molecular or turbulent (small-scale pulsations). The volumetric reactions are the mass sources (and sink) as a result of chemical reaction of SO_2 in the liquid and the interphase mass transfer.

A qualitative theoretical analysis of the absorption kinetics in the cases of two-phases absorbent, using the diffusion type of model [6, 10], will be presented.

Let's ε_1 and ε_2 are the gas and liquid/solid suspension parts in the medium elementary volume $(\varepsilon_1 + \varepsilon_2 = 1)$, i.e. gas and liquid /solid suspension holdup coefficients.

Considering that c_1 (c_2) is the concentration of SO_2 in the gas (liquid) phase and c_3 is the concentration of $CaCO_3$ in the absorbent, the mass sources (sink) in the medium elementary volume are equal to the rate of the chemical reaction $k_0 c_2 c_3$, the rate of the interphase mass transfer across the gas-liquid boundary $k(c_1 - \chi c_2)$ and the rate of the interphase mass transfer $k_1(c_3^0 - c_3)$ across the liquid-solid boundary, where c_3^0 is the maximal concentration (equilibrium solubility) of $CaCO_3$, k_0 - chemical reaction rate constant, k, k_1 - interphase mass transfer coefficients, χ - Henry's number. As a result the convection-diffusion equations in a column apparatus [6], for counter-current absorption process, will be presented in two coordinates systems $(z_1, r), (z_2, r), (z_1 + z_2 = l)$:

$$\varepsilon_1 u_1 \frac{\partial c_1}{\partial z_1} = \varepsilon_1 D_1 \left(\frac{\partial^2 c_1}{\partial z_1^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial r^2} \right) - k(c_1 - \chi c_2),$$

$$\varepsilon_2 u_2 \frac{\partial c_2}{\partial z_2} = \varepsilon_2 D_2 \left(\frac{\partial^2 c_2}{\partial z_2^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} + \frac{\partial^2 c_2}{\partial r^2} \right) + k(c_1 - \chi c_2) - k_0 c_2 c_3,$$

$$\varepsilon_2 u_2 \frac{\partial c_3}{\partial z_2} = \varepsilon_2 D_3 \left(\frac{\partial^2 c_3}{\partial z_2^2} + \frac{1}{r} \frac{\partial c_3}{\partial r} + \frac{\partial^2 c_3}{\partial r^2} \right) - k_0 c_2 c_3 + k_1(c_3^0 - c_3), \quad (1)$$

where $u_1(r), u_2(r)$ are velocity distributions in the gas and liquid, $c_i(z, r)$ and D_i $(i = 1, 2, 3)$ are the concentration distributions and the diffusivities of SO_2 in the gas and liquid and of $CaCO_3$ in the liquid.

The boundary conditions of (1) in column with a radius r_0 and working zone height l, for a counter-current gas-liquid drops flow, have the form:

$$z_1 = 0, \quad c_1(0, r) \equiv c_1^0, \quad \bar{u}_1 c_1^0 = u_1(r) c_1^0 - D_1 \left(\frac{\partial c_1}{\partial z_1} \right)_{z_1 = 0};$$

$$z_2 = 0, \quad c_2(0,r) \equiv c_2^0, \quad \bar{u}_2 c_2^0 = u_2(r) c_2^0 - D_2 \left(\frac{\partial c_2}{\partial z_2} \right)_{z_2=0};$$

$$z_2 = 0, \quad c_3(0,r) \equiv c_3^0, \quad \bar{u}_2 c_3^0 = u_2(r) c_3^0 - D_3 \left(\frac{\partial c_3}{\partial z_2} \right)_{z_2=0}; \quad (z_1 + z_2 = l);$$

$$r = 0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = \frac{\partial c_3}{\partial r} = 0; \qquad r = r_0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = \frac{\partial c_3}{\partial r} = 0, \tag{2}$$

where $\bar{u}_i$, c_i^0, $i = 1,2$, are the inlet average velocities and the inlet concentrations of SO_2 in the gas and liquid phases, c_3^0 is the maximal (equilibrium) solubility of $CaCO_3$. Practically $c_1^0 \sim 10^{-4}$ kgmol.m^{-3}, $c_2^0 = 0$, $c_3^0 \sim 10^{-4}$ kgmol.m^{-3} and Henry's number $\chi \sim 10^{-2}$.

2. Generalized analysis

A qualitative analysis of the model (1) is possible to be made, using dimensionless (generalized) variables [6]:

$$R = \frac{r}{r_0}, \quad Z_1 = \frac{z_1}{l}, \quad Z_2 = \frac{z_2}{Z_2}, \quad U_1 = \frac{u_1}{\bar{u}_1}, \quad U_2 = \frac{u_2}{\bar{u}_2}, \quad C_1 = \frac{c_1}{c_1^0}, \quad C_2 = \frac{c_2 \chi}{c_1^0}, \quad C_3 = \frac{c_3}{c_3^0}. \tag{3}$$

If put (3) into (1), the model in generalized variables has the form:

$$U_1 \frac{\partial C_1}{\partial Z_1} = \frac{D_1 l}{\bar{u}_1 r_0^2} \left(\frac{r_0^2}{l^2} \frac{\partial^2 C_1}{\partial Z_1^2} + \frac{1}{R} \frac{\partial C_1}{\partial R} + \frac{\partial^2 C_1}{\partial R^2} \right) - \frac{kl}{\varepsilon_1 \bar{u}_1} (C_1 - C_2),$$

$$U_2 \frac{\partial C_2}{\partial Z_2} = \frac{D_2 l}{\bar{u}_2 r_0^2} \left(\frac{r_0^2}{l^2} \frac{\partial^2 C_2}{\partial Z_2^2} + \frac{1}{R} \frac{\partial C_2}{\partial R} + \frac{\partial^2 C_2}{\partial R^2} \right) + \frac{kl \chi}{\varepsilon_2 \bar{u}_2} (C_1 - C_2) - \frac{k_0 l c_3^0}{\varepsilon_2 \bar{u}_2} C_2 C_3,$$

$$U_2 \frac{\partial C_3}{\partial Z_2} = \frac{D_3 l}{\bar{u}_2 r_0^2} \left(\frac{r_0^2}{l^2} \frac{\partial^2 C_3}{\partial Z_2^2} + \frac{1}{R} \frac{\partial C_3}{\partial R} + \frac{\partial^2 C_3}{\partial R^2} \right) - \frac{k_0 l c_1^0}{\varepsilon_2 \bar{u}_2 \chi} C_2 C_3 + \frac{k_l l}{\varepsilon_2 \bar{u}_2} (1 - C_3). \tag{4}$$

The using of the notations K, K_1 for the dimensionless chemical kinetic parameters in the mass transfer equations of SO_2 and $CaCO_3$ in (4), leads to:

$$K = \frac{k_0 l c_3^0}{\varepsilon_2 \bar{u}_2}, \quad K_1 = \frac{k_0 l c_1^0}{\varepsilon_2 \bar{u}_2 \chi}, \quad \frac{K}{K_1} = \frac{\chi c_3^0}{c_1^0} \sim 10^{-2}, \tag{5}$$

i.e. in the diffusion type of model (4), the chemical reaction effect on the interphase mass transfer of SO_2 is possible to be neglected (if $K_1 \leq 1, 0 = K \leq 10^{-2}$).

The presented theoretical analysis of the gas absorption with two-phases absorbent in counter-current gas-liquid drops flow shows, that the process is practically physical absorption (as a result of the low concentration of the dissolved $CaCO_3$ in the drops) and the mathematical model is possible to be obtained directly from the model (1, 2), where $c_2^0 = 0$, i.e.:

$$\varepsilon_1 u_1 \frac{\partial c_1}{\partial z_1} = \varepsilon_1 D_1 \left(\frac{\partial^2 c_1}{\partial z_1^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial r^2} \right) - k(c_1 - \chi c_2),$$

$$\varepsilon_2 u_2 \frac{\partial c_2}{\partial z_2} = \varepsilon_2 D_2 \left(\frac{\partial^2 c_2}{\partial z_2^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} + \frac{\partial^2 c_2}{\partial r^2} \right) + k(c_1 - \chi c_2);$$

$$z_1 = 0, \quad c_1(0,r) \equiv c_1^0, \quad \bar{u}_1 c_1^0 = u_1(r) c_1^0 - D_1 \left(\frac{\partial c_1}{\partial z_1} \right)_{z_1=0};$$

$$z_2 = 0, \quad c_2(0,r) \equiv 0, \quad \left(\frac{\partial c_2}{\partial z_2} \right)_{z_2=0} = 0; \quad (z_1 + z_2 = l);$$

$$r = 0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = 0; \quad r = r_0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} = 0. \tag{6}$$

The chemical reaction rate between SO_2 and dissolved $CaCO_3$ occurs in the collected absorbent in the bottom half of the column only.

3. Average concentration model

In the diffusion type model (6), the velocity distributions in the phases cannot be obtained, because the equation of the interphase surface is not possible to be obtained. The problem can be avoided if the average values of the velocity and concentration over the cross-sectional area of the column are used, i.e. the medium elementary volume will be equivalent to the cylinder with radius r_0 and a height, which is sufficiently small with respect to the column height l and at the same time sufficiently large with respect to the intermolecular volumes in the medium.

This new approach is more adequate with respect to the experimental data commonly used for the purpose of parameter identification, because measurements of average values (velocity or concentration) are simpler with respect to local (point) measurements.

The average values of the velocity and concentration for the column cross-sectional area is possible to be obtained [6], using the expressions:

$$\bar{u}_i = \frac{2}{r_0^2} \int_0^{r_0} r u_i(r) dr, \quad \bar{c}_i(z_i) = \frac{2}{r_0^2} \int_0^{r_0} r c_i(r, z_i) dr, \quad i = 1,2. \tag{7}$$

The velocity and concentration distributions in (6) can be represented with the help of the average functions (7):

$$u_i(r) = \bar{u}_i \tilde{u}_i(r), \quad c_i(r, z_i) = \bar{c}_i(z_i) \, \tilde{c}_i(r, z_i), \quad i = 1,2. \tag{8}$$

Here $\tilde{u}_i(r)$, $\tilde{c}_i(r, z_i)$, $i = 1,2$ represent the radial nonuniformity of both the velocity and the concentration distributions, satisfying the conditions:

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_i(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_i(r, z_i) dr = 1, \quad i = 1,2. \tag{9}$$

The average concentration model may be obtained [6] if put (8) into (6) and then multiply by r and integrate with respect to r over the interval $[0, r_0]$. The result is:

$$\alpha_i(z_i) \bar{u}_i \frac{d\bar{c}_i}{dz_i} + \frac{d\alpha_i}{dz_i} \bar{u}_i \bar{c}_i = D_i \frac{d^2\bar{c}_i}{dz_i^2} - (-1)^{i+1} \frac{k}{\varepsilon_i} (\bar{c}_1 - \chi \bar{c}_2);$$

$$z_1 = 0, \quad \bar{c}_1(0) = c_1^0, \quad \left(\frac{d\bar{c}_1}{dz_1} \right)_{z_1=0} = 0;$$

$$z_2 = 0, \quad \bar{c}_2 = 0, \quad \left(\frac{d\bar{c}_2}{dz_2} \right)_{z_2=0} = 0; \quad i = 1,2, \tag{10}$$

where

$$\alpha_i = \frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_i \tilde{c}_i dr, \quad i = 1,2. \tag{11}$$

The using of generalized variables:

$$z_i = l Z_i, \quad i = 1,2, \quad \bar{c}_1 = c_1^0 \bar{C}_1, \quad \bar{c}_2 = \frac{c_1^0}{\chi} \bar{C}_2, \tag{12}$$

leads to

$$A_i \frac{d\bar{C}_i}{dZ_i} + \frac{dA_i}{dZ_i}\bar{C}_i = Pe_i^{-1} \frac{d^2\bar{C}_i}{dZ_i^2} - (-1)^{i+1} K_i\left(\bar{C}_1 - \bar{C}_2\right), \quad i = 1,2;$$

$$Z_i = 0, \quad \bar{C}_1 = 1, \quad \bar{C}_2 = 0, \quad \left(\frac{d\bar{C}_i}{dZ_i}\right)_{Z_i=0} = 0, \quad i = 1,2, \tag{13}$$

where

$$Pe_i = \frac{\bar{u}_i l}{D_i}, \quad K_i = \frac{k l \chi^{i-1}}{\varepsilon_i \bar{u}_i}, \quad \alpha_i(z_i) = \alpha_i(lZ_i) = A_i(Z_i), \quad i = 1,2. \tag{14}$$

In (13) the model parameters $0 = Pe_i^{-1} \ll 10^{-2}, i = 1,2$ and (13) lead to:

$$A_i \frac{d\bar{C}_i}{dZ_i} + \frac{dA_i}{dZ_i}\bar{C}_i = -(-1)^{i+1} K_i\left(\bar{C}_1 - \bar{C}_2\right); \quad Z_i = 0, \quad \bar{C}_1 = 1, \quad \bar{C}_2 = 0, \quad i = 1,2. \tag{15}$$

In [11] was shown, that for the functions $A_i(Z_i), i = 1,2$, is possible to be used linear approximations:

$$A_i = 1 + a_i Z_i, \quad i = 1,2 \tag{16}$$

and as a result (15) have the form:

$$\left(1 + a_i Z_i\right)\frac{d\bar{C}_i}{dZ_i} + a_i \bar{C}_i = (-1)^i K_i\left(\bar{C}_1 - \bar{C}_2\right), i = 1,2; \ Z_1 = 0, \ \bar{C}_1 = 1; \ Z_2 = 0, \ \bar{C}_2 = 0. \tag{17}$$

4. Algorithm of the solution

An iterative solutions of (17) will be presented as two matrix forms and its polynomial approximations:

$$\bar{C}_1^{(t)}(Z_1) = \left\|\bar{C}_{\hat{z}_1}^{(t)}\right\| = \sum_{i=1}^{5} \left\|\bar{a}_{(i-1)}^{(t)}\right\| Z_1^{(i-1)}, \quad Z_1 = 0.01\hat{z}_1, \quad \hat{z}_1 = 1,2,...,100. \tag{18}$$

$$\bar{C}_2^{(t)}(Z_2) = \left\|\bar{C}_{\hat{z}_2}^{(t)}\right\| = \sum_{i=1}^{5} \left\|\bar{\alpha}_{(i-1)}^{(t)}\right\| Z_2^{(i-1)}, \quad Z_2 = 0.01\hat{z}_2, \quad \hat{z}_2 = 1,2,...,100. \tag{19}$$

In (18,19) $t = 1,2,...,t_0$ is the iterative number and $\bar{C}_1^{(t)}(Z_1) = \left\|\bar{C}_{\hat{z}_1}^{(t)}\right\|$ and $\bar{C}_2^{(t)}(Z_2) = \left\|\bar{C}_{\hat{z}_2}^{(t)}\right\|$ are consecutive solutions of the problems:

$$\left(1 + a_2 Z_2\right)\frac{d\bar{C}_2^{(t)}}{dZ_2} + a_2 \bar{C}_2^{(t)} = K_2\left(\hat{C}_1^{(t-1)} - \bar{C}_2^{(t)}\right), \quad Z_2 = 0, \quad \bar{C}_2 = 0. \tag{20}$$

$$\left(1 + a_1 Z_1\right)\frac{d\bar{C}_1^{(t)}}{dZ_1} + a_1 \bar{C}_1^{(t)} = -K_1\left(\bar{C}_1^{(t)} - \hat{C}_2^{(t)}\right), \quad Z_1 = 0, \quad \bar{C}_1^{(t)} = 1. \tag{21}$$

In (20, 21) are used the functions:

$$\hat{C}_1^{(t-1)}(Z_2) = \bar{C}_1^{(t-1)}(Z_1 = 1 - Z_2) = \sum_{i=1}^{5} \left\| \bar{a}_{(i-1)}^{(t-1)} \right\| (1 - Z_2)^{(i-1)}. \tag{22}$$

$$\hat{C}_2^{(t-1)}(Z_1) = \bar{C}_2^{(t-1)}(Z_2 = 1 - Z_1) = \sum_{i=1}^{5} \left\| \bar{\alpha}_{(i-1)}^{(t-1)} \right\| (1 - Z_1)^{(i-1)}. \tag{23}$$

The zero iteration uses the matrix:

$$\hat{C}_1^{(0)}(Z_2) = \bar{C}_1^{(0)}(Z_1) = \left\| \bar{C}_{\hat{z}_1}^{(0)} \right\| \equiv 1 \tag{24}$$

and the first iteration starts with the solution of the equation:

$$\left(1 + a_2 Z_2\right) \frac{d\bar{C}_2^{(1)}}{dZ_2} + a_2 \bar{C}_2^{(1)} = K_2 \left(1 - \bar{C}_2^{(1)}\right), \quad Z_2 = 0, \quad \bar{C}_2^{(1)} = 0. \tag{25}$$

The stop criterion is the condition:

$$\frac{1}{100} \sum_{\hat{z}_1=1}^{100} \left(\left\| \bar{C}_{\hat{z}_1}^{(t_0)} \right\| - \left\| \bar{C}_{\hat{z}_1}^{(t_0-1)} \right\| \right) \le 10^{-3}. \tag{26}$$

where t_0 is the last iteration number.

5. Parameters identification

The parameters $a_i, K_i, i = 1, 2$ in the model (17) will be obtained on the bases of 10 experimental values of $\bar{C}_1^{\exp}(Z_1)$ for different values of Z_1:

$$\bar{C}_1^{\exp}(Z_1) = \left\| \bar{C}_{\zeta j}^{\exp} \right\|, \quad Z_1 = 0.1\zeta, \quad \zeta = 1, 2, 3, \quad j = 1, 2, ..., 10. \tag{27}$$

The parameter identification in the average concentration model (17) will be made by the minimization of the least-squares function:

$$Q_\zeta\left(a_{1\zeta}, a_{2\zeta}, K_{1\zeta}, K_{2\zeta}\right) = \sum_{j=1}^{10} \left[\left(\bar{C}_\zeta^{(t_0)} - \bar{C}_{\zeta j}^{\exp} \right)^2 \right], \quad \zeta = 1, 2, 3.$$

It was shown [18], that the experimental data for $\zeta = 1$ or $\zeta = 2$ are sufficient for the identification of the parameters $a_i, K_i, i = 1, 2$.

Conclusions

The presented theoretical analysis of the method, which is used from many companies for waste gases purification from SO_2, using two-phase absorbents ($CaCO_3$ suspension), for waste gases purification from SO_2, has a number of shortcomings:

1. The process efficiency is very small because the absorption rate is limited by the physical absorption of SO_2 in water.

2. The chemical reaction of $CaCO_3$ with SO_2 lead to CO_2 emission (every molecule of SO_2, absorbed from the air, is equivalent to a molecule of CO_2, emitted in the air) and this is a new ecological problem, because the greenhouse effects of SO_2 and CO_2 are similar.

3. The large quantity of by-products (gypsum) is a problem too.

4. The impossibility for regeneration of the absorbents.

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