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\textsubscript{2} concentration [1].

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 $c_0 - c^*$, where $c_0$ is SO\textsubscript{2} concentration in the gas volume and $c^*$ is SO\textsubscript{2} concentration at the gas-liquid interphase [2, 3]. A maximal absorption rate is possible if $c^* = 0$, i.e. in the cases of irreversible chemical reactions of SO\textsubscript{2} in liquid phase.

The irreversible chemical reactions in the liquid phase, using alkaline absorbents (solutions of NaOH, Na\textsubscript{2}CO\textsubscript{3}, NH\textsubscript{4}OH) affect significantly the gas-liquid interphase mass transfer [4, 5]. Depending on the reaction rate the interphase mass transfer mechanism may be changed and in many cases this affects the limiting stage of the process. The increase of the reaction rate leads to consequent augmentation of the interphase mass transfer rate [2, 3].

The gas absorption complicated with a chemical reaction in the liquid phase is possible to be used for SO\textsubscript{2} absorption in packed bed columns. Taking into account the small dimensions of the packing elements the mass transfer occurs in a thin liquid layers near the interphase surface. Because of that the diffusion boundary layer theory [6, 7] is widely used for the analysis of the chemical reaction effects in the liquid phase on the interphase mass transfer mechanism.

The using of alkaline absorbents (solutions of NaOH, Na\textsubscript{2}CO\textsubscript{3}, NH\textsubscript{4}OH) is very expensive [8], i.e. the purification of huge amounts of waste gases of the thermal power plants needs of inexpensive reagents (CaCO\textsubscript{3}...
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) [9].

Diffusion type of model

The diffusion type of models [7-9] is possible to be used for the modeling of the gas absorption processes in column apparatuses. In the cases of two phase absorbents will be considered a moving gas - liquid dispersion in column apparatus, where a SO2 absorption with CaCO3/H2O suspension is realized.

The base of the model will be the convection-diffusion equation in the approximations of the mechanics of continua [7], 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.

Let $e_1$ and $E_2$ are the gas and liquid/solid suspension parts in the medium elementary volume ($s, +e_2 = 1$) and $c_1, (c_2)$ is the concentration of SO2 in the gas (liquid) phase and $c_3$ is the concentration of CaCO3 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 $k(c_1 - \%c_2)$ and the rate of the interphase mass transfer over the liquid-solid boundary, where $c_3^*$ is the maximal (equilibrium) solubility of CaCO3. As a result the convection-diffusion equations in a column apparatus have the form:

\[
\begin{align*}
\varepsilon_1 u_1 \frac{\partial c_1}{\partial t} &= -\varepsilon_1 D_1 \left( \frac{\partial^2 c_1}{\partial z^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial r^2} \right) - k(c_1 - \%c_2), \\
\varepsilon_2 u_2 \frac{\partial c_2}{\partial t} &= -\varepsilon_2 D_2 \left( \frac{\partial^2 c_2}{\partial z^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} + \frac{\partial^2 c_2}{\partial r^2} \right) - k(c_1 - \%c_2),
\end{align*}
\]
where \( u_1(r), u_2(r) \) are velocity distributions in the gas and liquid (symmetric with respect to the longitudinal coordinate \( z \)), \( C_j(z,r) \) and \( D_j \) \( (i = 1, 2, 3) \) are the concentration distributions and the diffusivities of SO2 in the gas and liquid and of CaCO3 in the liquid, \( k_0 \) - chemical reaction rate constant, \( k, ^\gamma \) - interphase mass transfer coefficients.

Let us consider a co-current gas-liquid bubble column with a radius \( r_0 \) and working zone height \( l \). The boundary conditions of (1) have the form [8, 9]:

\[
\begin{align*}
  z = 0, & \quad \left. (0, 1-)^\circ, \quad D_1 c_1^0 = u_1(r)c_1(0, r) - D_1 f^\gamma \right|_{z = 0}; \\
  z = 0, & \quad \left. c_2(0, r) = c_2^\circ, \quad u_2 c_2^\circ = u_2(r)c_2(0, r) - D_2 \frac{\partial c_2}{\partial z} \right|_{z = 0}; \\
  z = 0, & \quad \left. c_3(0, r) = c_3^\circ, \quad u_2 c_3^\circ = u_2(r)c_3(0, r) - D_3 \frac{\partial c_3}{\partial z} \right|_{z = 0}; \\
  r = 0, & \quad \left. \frac{\partial }{\partial x} \right|_{r = 0} = \left. \frac{\partial }{\partial x} \right|_{r = 0} = \left. \frac{\partial }{\partial x} \right|_{r = 0} = 0,
\end{align*}
\]

where \( \bar{u}_j c_j^0 \), \( i = 1, 2 \), are the inlet average velocities and the inlet concentrations in the gas and liquid phases. Practically \( c_j^0 = 0 \).

A qualitative analysis of the model (1) is possible to be made, using dimensionless (generalized) variables [9]. The low SO2 concentration \( (c^?) \) in the waste gases of the thermal power plants, in comparison with low the concentration of CaCO3 in the absorbent \( (c_3^0) \) and Henry's number \( (x \sim 10^7) \) show, that the mass transfer resistance is distributed in the gas and liquid phases and lead to the necessity of solution of the full set of equations (1, 2).
Average Concentration Model

Generally, in the diffusion-type model (1) and (2), 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 column radius and a height, which is sufficiently small with respect to the column height and at the same time sufficiently large with respect to the intermolecular distances in the medium.

This 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.

In our book [7] was shown, that the diffusion type of models are a base for the average concentration models creations. This approach is possible to be applied for introducing average velocities and concentrations in (1,2).

The average values of the velocity and concentration for the column cross-sectional area can be obtained [8, 9], using the expressions:

\[ \bar{u}_i = \frac{2}{\pi} \int_0^a u_i(r) \, dr, \quad \bar{c}_i \, \phi = \frac{2}{\pi} \int_0^b c_i(r,z) \, dr, \quad i = 1,2,3. \]  

The velocity and concentration distributions in (1, 2) can be represented with the help of the average functions (3):

\[ \phi(r) = \bar{u}_i \, \bar{\eta}'(r), \quad c_i(r,z) = \bar{c}_i ; (z) c_i (r,z), \quad i = 1,2,3. \]  

Here \( \bar{\eta} \), \( \bar{D} \), \( \bar{c}_i (r,z) \), \( i = 1,2,3 \) represent the radial nonuniformity of both the velocity and the concentration distributions, satisfying the conditions:

\[ 4 \int_0^r u_i (r,z) \, dr = 1, \quad 4 \int_0^r c_i (r,z) \, dr = 1, \quad i = 1,2,3. \]  

The average concentration model can be obtained if put (4) into equations (1, 2) and then multiply every equation by \( r \) and integrate with respect to \( r \) over the interval \([0, \, r_{\text{eq}}] \). The result is:
In (6-8) the radial non-uniformities in the velocity and concentration distributions are presented by:

\[ o_i(z) = \left( 1 \right)^i \left( \int_0^1 \bar{c} \right) (r.2)^i, \quad i = 1, 2; \]

\[ a_3(z) = \int_0^1 \int_0^r \int_0^z \bar{c} \, r \, dr \, dl \, dz, \quad P_3 = \int_0^z \frac{d \alpha_3}{dl}, \quad y(z) = \int_0^z \frac{d \alpha_3}{dl} \, dz. \] (9)

The parameters in the average concentration model represent the radial non-uniformity of the velocity and concentration and is possible to be obtained using experimental data. As a result, a modeling of the absorption columns in the cases of two-phase (solid-liquid) absorbents is possible.

Conclusions

The presented theoretical analysis shows that the low SO2 concentration in the waste gases of the thermal power plants needs an
irreversible chemical reactions of SO2 with alkaline reagents in the liquid phase in case of gas-liquid dispersion system. For the purification of huge amounts of waste gases must be used inexpensive reagents (CaCO3 suspension). The presence of the active component in the absorbent as both a solution and solid phase leads to an increase of the absorption capacity of the absorbent, but the introduction of a new process (the dissolution of the solid phase) creates conditions for a variation of the absorption mechanism (interphase mass transfer through two interphase surfaces - gas/liquid and liquid/solid). At these conditions the mass transfer resistance is distributed in the both phases, i.e. the convection-diffusion equations of SO2 (in gas and liquid phases) and CaCO3 (in liquid phase) must be solved together.

The impossibility for the solution of the convection-diffusion equations in gas-liquid dispersion system leads to the necessity of using a diffusion type of models, where the velocity and concentration distributions in column apparatuses are replaced by the average values of the velocity and concentration over the cross-sectional area of the column. The parameters in these type of models replace the effects, the radial non-uniformities of the velocity and the concentration distributions at the cross-sectional area of the column. They can be obtained, using experimental data.

References
