

On the SO₂ Problem in Thermal Power Plants. 1. Absorption processes modeling

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Abstract: A theoretical analysis, of the processes for gas purification from low SO₂ concentration in the thermal power plants, is presented. A new approach, for qualitative analysis (convection-diffusion type of model) and quantitative description (average concentration model) of the absorption processes in column apparatuses, is proposed. The theoretical analysis of the physical absorption, chemical absorption and absorption with two-phase absorbent, is shown. The presented theoretical analysis of the methods and apparatuses for waste gases purification from SO₂, using two-phase absorbent (CaCO₃ suspension), shows, that the process is physical absorption practically and the mass transfer resistances in the gas and liquid phases are 44% and 56% respectively. In these conditions a new patent is proposed, where the process optimization is realized in two-zone column, where the upper zone is physical absorption in gas-liquid drops system and the lower zone is physical absorption in liquid-gas bubbles system. The chemical reaction takes place in the column tank.

Keywords: gas purification, physical absorption, chemical absorption, two-phase absorbent, mass transfer resistance, convection-diffusion model, average concentration model.

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 SO₂ concentration [1-4]. The huge gas amounts need big apparatuses size, which is possible to be decreased if the purification process rate is maximal.

Practically, the waste gases purification from SO₂ in the thermal power plants uses absorption methods [5], [6]. The absorption kinetics modeling use the model theories of the mass transfer as the film theory [7], penetration theory [8], surface renewal theory [9], [10], [11]. These theories do not lead to good results because they do not use the actual distribution of velocities around the gas-liquid phase boundary. This disadvantage is removed in the diffusion boundary layer theory [12], but it is also not applicable for modeling of the absorption kinetics in the column apparatuses, where the local velocities in the flows are unknown and can not be determined, practically.

The SO₂ absorption intensification needs a quantitative description of the process, using a suitable mathematical model [13-17], which must be created on the base of a qualitative analysis of the process mechanism.

A theoretical analysis of the methods and apparatuses for waste gases purification from SO₂, using two-phase absorbent (CaCO₃ suspension) [18-20], from some companies (Babcock & Wilcox Power Generation Group, Inc., Alstom Power Italy, Idreco-

Insigma-Consortium) in the thermal power plants, will be presented.

The gas absorption is practically realized in column apparatuses, where two phases' gas-liquid flows are very often gas-liquid drops or liquid-gas bubbles dispersed systems. The absorption rate is related with the interphase mass transfer resistance, which is disturbed between the gas and liquid phases in the column. The absorption rate increase is possible to be realized if the mass transfer resistance in the limiting phase (phase with the higher resistance) decrease as a result of the intensification of the convective transfer, because the role of the diffusion mass transfer is much smaller.

In gas-liquid dispersed systems the convective transfer in the dispersion phase (drops, bubbles) is very limited. As a result the optimal realization of the absorption processes, where the interphase mass transfer is limited by the mass transfer in the gas phase, are the gas-liquid drops columns, while in the opposite case the liquid-gas bubbles columns are optimal.

The modeling of the absorption processes in column apparatuses is difficult, because the finding of the velocities distributions in the phases and the interphase surface is impossible, practically. The interphase mass transfer processes in column apparatuses is possible to be modeled, using a new approach on the base of the approximations of the mechanics of continua [13-17], 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 volumes of the medium.

The using of the convection-diffusion type of models for a quantitative description of the gas absorption in column apparatuses is not possible because the velocity functions in the convection-diffusion equations are unknown. The problem can be avoided if the average values of the velocities and concentrations over the cross-sectional area of the column are used [13-17], i.e. the medium elementary volume (in the physical approximations of the mechanics of continua) will be equivalent to a small cylinder with real 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.

1. Physical absorption

The first step of the absorption process modeling is the process mechanism identification. This theoretical analysis is possible to be made in the approximations of the mechanics of continua [13-17].

1.1. Convection-diffusion type of model

The gas absorption process practically is possible to be realized in gas-liquid dispersion, moving in column apparatuses, where the dispersed phase is liquid drops or gas bubbles. In these hydrodynamic conditions the velocity distributions in the gas and liquid phases in the column is not possible to be obtained and a qualitative theoretical analysis of the absorption kinetics, using the diffusion type of model [13-17], is possible to be made only.

Let's consider a moving gas-liquid dispersion in column apparatus, where a physical absorption of SO₂ with water is realized. The mathematical model of the process will be created in the approximations of the mechanics of continua [13]. The base of the model will be the convection-diffusion equation [13-17], where the convective transfer in the medium elementary volume results from laminar or turbulent (as a result of large-scale pulsations) flows, the diffusive transfer is molecular or turbulent (as a result of small-scale pulsations) and the interphase mass transfer is a volume reaction (creation or disappearance of a substance).

Let's consider a co-current gas-liquid dispersion column, where ω_G and ω_L are the gas and liquid parts in the medium elementary volume ($\omega_G + \omega_L = 1$), i.e. gas and liquid holdup coefficients. If c_G, c_L are the concentrations [kg-mol.m⁻³] of SO₂ in the gas and liquid phases, the mass source (sink) in the medium elementary volume is equal to the rate of the interphase mass transfer $k(c_G - \chi c_L)$. As a result the convection-diffusion equations in a column apparatus in cylindrical coordinate system (z, r) have the form:

$$\begin{aligned} \omega_G u_G \frac{\partial c_G}{\partial z} &= \omega_G D_G \left(\frac{\partial^2 c_G}{\partial z^2} + \frac{1}{r} \frac{\partial c_G}{\partial r} + \frac{\partial^2 c_G}{\partial r^2} \right) - k(c_G - \chi c_L), \\ \omega_L u_L \frac{\partial c_L}{\partial z} &= \omega_L D_L \left(\frac{\partial^2 c_L}{\partial z^2} + \frac{1}{r} \frac{\partial c_L}{\partial r} + \frac{\partial^2 c_L}{\partial r^2} \right) + k(c_G - \chi c_L), \end{aligned} \quad (1)$$

where $u_G(r), u_L(r)$ are velocity distributions in the gas and liquid (symmetric with respect to the longitudinal coordinate z , i.e. the radial velocity components are equal to zero [13-17]), $c_G(z, r), c_L(z, r)$ and D_G, D_L are the concentration distributions and the diffusivities of SO₂ in the gas and liquid, k - interphase mass transfer coefficient. For a column with radius r_0 and working zone height l , the boundary conditions of (1) have the form:

$$\begin{aligned} z=0, \quad c_G(0, r) &\equiv c_G^0, \quad u_G^0 c_G^0 \equiv u_G(r) c_G^0 - D_G \left(\frac{\partial c_G}{\partial z} \right)_{z=0}; \\ z=0, \quad c_L(0, r) &\equiv c_L^0, \quad u_L^0 c_L^0 \equiv u_L(r) c_L^0 - D_L \left(\frac{\partial c_L}{\partial z} \right)_{z=0}; \\ r=0, \quad \frac{\partial c_G}{\partial r} &= \frac{\partial c_L}{\partial r} \equiv 0; \quad r=r_0, \quad \frac{\partial c_G}{\partial r} = \frac{\partial c_L}{\partial r} \equiv 0, \end{aligned} \quad (2)$$

where $u_G^0, u_L^0, c_G^0, c_L^0$ are the inlet ($z=0$) average velocities and

concentrations in the gas and liquid phases (practically $c_L^0 = 0$).

The using of dimensionless (generalized) variables [13-17] permit to be made a qualitative analysis of the model (1), (2), where as characteristic scales are used average velocities, inlet concentrations and column parameters:

$$\begin{aligned} R &= \frac{r}{r_0}, \quad Z = \frac{z}{l}, \quad U_G = \frac{u_G}{u_G^0}, \quad U_L = \frac{u_L}{u_L^0}, \\ C_G &= \frac{c_G}{c_G^0}, \quad C_L = \frac{c_L \chi}{c_G^0}, \quad \varepsilon = \frac{r_0^2}{l^2} \end{aligned} \quad (3)$$

If put (3) in (1), (2), the model in generalized variables has the form:

$$\begin{aligned} U_G \frac{\partial C_G}{\partial Z} &= Fo_G \left(\varepsilon \frac{\partial^2 C_G}{\partial Z^2} + \frac{1}{R} \frac{\partial C_G}{\partial R} + \frac{\partial^2 C_G}{\partial R^2} \right) - \\ &- \frac{kl}{\omega_G u_G^0} (C_G - C_L); \\ U_L \frac{\partial C_L}{\partial Z} &= Fo_L \left(\varepsilon \frac{\partial^2 C_L}{\partial Z^2} + \frac{1}{R} \frac{\partial C_L}{\partial R} + \frac{\partial^2 C_L}{\partial R^2} \right) + \\ &+ \frac{kl \chi}{\omega_L u_L^0} (C_G - C_L); \\ Z=0, \quad C_G(0, R) &\equiv 1, \quad 1 \equiv U_G(R) - Pe_G^{-1} \left(\frac{\partial C_G}{\partial Z} \right)_{z=0}; \\ Z=0, \quad C_L(0, R) &\equiv 0, \quad 1 \equiv U_L(R) - Pe_L^{-1} \left(\frac{\partial C_L}{\partial Z} \right)_{z=0}; \\ R=0, \quad \frac{\partial C_G}{\partial R} &= \frac{\partial C_L}{\partial R} \equiv 0; \quad R=1, \quad \frac{\partial C_G}{\partial R} = \frac{\partial C_L}{\partial R} \equiv 0; \end{aligned} \quad (4)$$

where Fo_G, Fo_L and Pe_G, Pe_L are Fourier and Peclet numbers:

$$Fo_G = \frac{D_G l}{u_G^0 r_0^2}, \quad Fo_L = \frac{D_L l}{u_L^0 r_0^2}, \quad Pe_G = \frac{u_G^0 l}{D_G}, \quad Pe_L = \frac{u_L^0 l}{D_L}. \quad (5)$$

In (5) the dimensionless parameter $Fo = Dl/u^0 r_0^2$ (like the Fourier number) is possible to be presented as $Fo = Pe^{-1} \varepsilon^{-1}$, but Pe and ε (in this case) do not present separate physical effects.

The use of the dimensionless (generalized) variables in the model equations (where as variables scales are used the maximal or average variable values), lead to the model, where the unity is the order of magnitude of all functions and their derivatives, i.e. the effects of the physical and chemical phenomena (the contribution of the terms in the model) are determined by the orders of magnitude of the dimensionless parameters in the model equations. If all equations in the model are divided by the dimensionless parameter, which have the maximal order of magnitude, all terms in the model equations will be classified in three parts:

1. The parameter is one or its order of magnitude is one, i.e. this mathematical operator represents a main physical effect;
2. The parameter's order of magnitude is 10^{-1} , i.e. this mathematical operator represents a small physical effect;
3. The parameter's order of magnitude is $\leq 10^{-2}$, i.e. this mathematical operator represents a very small (negligible) physical effect, which must be neglected, because this effect is not possible to be measured experimentally.

For example, if in the high column the parameter ε is very small ($\varepsilon \leq 10^{-2}$), in the model (4) is possible to be replaced $\varepsilon = 0$, i.e. $0 = \varepsilon \leq 10^{-2}$.

From (4) it follows, that as dimensionless mass transfer resistances in the gas (ρ_G) and liquid (ρ_L) phases is possible to be used:

$$\rho_G = \frac{kl}{\omega_G u_G^0}, \quad \rho_L = \frac{kl\chi}{\omega_L u_L^0}, \quad \phi \rho_G = \rho_L, \quad \rho_G + \rho_L = 1, \quad (6)$$

$$\rho_G = \frac{1}{1+\phi}, \quad \rho_L = \frac{\phi}{1+\phi}, \quad \phi = \frac{\omega_G u_G^0 \chi}{\omega_L u_L^0}.$$

In the cases of $\phi \rightarrow \infty$, $\rho_G = 0$, $C_G \equiv 1$ and interphase mass transfer is limited by the mass transfer in the liquid phase (the absorption must be realized in liquid-gas bubbles systems), while in the opposite case $\phi = 0$, $\rho_L = 0$, $C_L \equiv 0$ and interphase mass transfer is limited by the mass transfer in the gas phase (the absorption must be realized in gas-liquid drops systems).

In a real case of SO_2 physical absorption in gas-liquid drops system

$\chi = 2.55 \cdot 10^{-2}$, $\omega_G = 0.98$, $\omega_L = 0.02$, $u_G^0 = u_L^0 = 4 [m.s^{-1}]$,
 $\phi = 1.25$, $\rho_G = 0.444$, $\rho_L = 0.556$, i.e. the interphase mass transfer resistances in the gas (44.4%) and liquid (55.6%) phases are commensurate.

In (4) is possible to be used the approximation $0 = \varepsilon \leq 10^{-2}$ and to be obtained the high columns model:

$$U_G \frac{\partial C_G}{\partial Z} = \text{Fo}_G \left(\frac{1}{R} \frac{\partial C_G}{\partial R} + \frac{\partial^2 C_G}{\partial R^2} \right) - \frac{kl}{\omega_G u_G^0} (C_G - C_L),$$

$$U_L \frac{\partial C_L}{\partial Z} = \text{Fo}_L \left(\frac{1}{R} \frac{\partial C_L}{\partial R} + \frac{\partial^2 C_L}{\partial R^2} \right) + \frac{kl\chi}{\omega_L u_L^0} (C_G - C_L); \quad (7)$$

$$Z = 0, \quad C_G(0, R) \equiv 1, \quad C_L(0, R) \equiv 0;$$

$$R = 0, \quad \frac{\partial C_G}{\partial R} = \frac{\partial C_L}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C_G}{\partial R} = \frac{\partial C_L}{\partial R} \equiv 0.$$

The Fourier numbers (Fo_G , Fo_L) in (4) permit to be made a qualitative analysis of the convective transfer and diffusive transfer effects. In many practical cases (as a result of a small value of the diffusivity and a big value of the average velocity)

$0 = \text{Fo}_G \leq 10^{-2}$, $0 = \text{Fo}_L \leq 10^{-2}$, i.e. the diffusion transfer is negligible, compared to the convective one, and the model (4) has the convective form:

$$U_G \frac{\partial C_G}{\partial Z} = -\frac{kl}{\omega_G u_G^0} (C_G - C_L), \quad U_L \frac{\partial C_L}{\partial Z} = \frac{kl\chi}{\omega_L u_L^0} (C_G - C_L); \quad (8)$$

$$Z = 0, \quad C_G(0, R) \equiv 1, \quad C_L(0, R) \equiv 0.$$

1.2. Average concentration model

The using of the convection-diffusion type of models for a quantitative description of the physical absorption in column apparatuses is not possible because the velocity functions in the convection-diffusion equations are unknown and average concentration models will be used (in the physical approximations of the mechanics of continua) [13-17].

The average velocity and concentration at the column cross-sectional area can be presented as:

$$\bar{u}_G = \frac{2}{r_0^2} \int_0^{r_0} r u_G(r) dr, \quad \bar{c}_G(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_G(r, z) dr, \quad (9)$$

$$\bar{u}_L = \frac{2}{r_0^2} \int_0^{r_0} r u_L(r) dr, \quad \bar{c}_L(z) = \frac{2}{r_0^2} \int_0^{r_0} r c_L(r, z) dr.$$

The velocities and concentration distributions in (1), (2) assume to be presented [13] by the average functions (9):

$$u_G(r) = \bar{u}_G \tilde{u}_G(r), \quad c_G(r, z) = \bar{c}_G(z) \tilde{c}_G(r, z), \quad (10)$$

$$u_L(r) = \bar{u}_L \tilde{u}_L(r), \quad c_L(r, z) = \bar{c}_L(z) \tilde{c}_L(r, z),$$

where $\tilde{u}_G(r)$, $\tilde{u}_L(r)$ and $\tilde{c}_G(r, z)$, $\tilde{c}_L(r, z)$ represent the radial non-uniformity of both the velocity and the concentration distributions, satisfying the conditions:

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_G(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_G(r, z) dr = 1, \quad (11)$$

$$\frac{2}{r_0^2} \int_0^{r_0} r \tilde{u}_L(r) dr = 1, \quad \frac{2}{r_0^2} \int_0^{r_0} r \tilde{c}_L(r, z) dr = 1.$$

The average concentration model may be obtained [13-17] if put the expressions (10) into the model equations (1), (2) and then multiply by r and integrate with respect to r over the interval $[0, r_0]$. The result is:

$$\alpha_G \frac{d\bar{c}_G}{dz} + \frac{d\alpha_G}{dz} \bar{c}_G = \frac{D_G}{\bar{u}_G} \frac{d^2 \bar{c}_G}{dz^2} - \frac{k}{\omega_G \bar{u}_G} (\bar{c}_G - \chi \bar{c}_L);$$

$$z = 0, \quad \bar{c}_G(0) = c_G^0, \quad \frac{d\bar{c}_G}{dz} = 0; \quad (12)$$

$$\alpha_L \frac{d\bar{c}_L}{dz} + \frac{d\alpha_L}{dz} \bar{c}_L = \frac{D_L}{\bar{u}_L} \frac{d^2 \bar{c}_L}{dz^2} + \frac{k}{\omega_L \bar{u}_L} (\bar{c}_G - \chi \bar{c}_L);$$

$$z = 0, \quad \bar{c}_L(0) = 0, \quad \frac{d\bar{c}_L}{dz} = 0;$$

where

$$\alpha_G = \alpha_G(z) = \frac{2}{r_0^2} \int_0^{r_0} r \bar{u}_G(r) \bar{c}_G(r, z) dr, \quad (13)$$

$$\alpha_L = \alpha_L(z) = \frac{2}{r_0^2} \int_0^{r_0} r \bar{u}_L(r) \bar{c}_L(r, z) dr.$$

The using of the generalized variables:

$$Z = \frac{z}{l}, \quad \bar{C}_G = \frac{\bar{c}_G}{c_G^*}, \quad \bar{C}_L = \frac{\bar{c}_L \chi}{c_G^*}, \quad \text{Pe}_G = \frac{\bar{u}_G l}{D_G},$$

$$\text{Pe}_L = \frac{\bar{u}_L l}{D_L}, \quad \bar{K}_G = \frac{k}{\omega_G \bar{u}_G}, \quad \bar{K}_L = \frac{k}{\omega_L \bar{u}_L}, \quad (14)$$

$$\alpha_G(z) = \alpha_G(lZ) = A_G(Z), \quad \alpha_L(z) = \alpha_L(lZ) = A_L(Z),$$

leads to:

$$A_G \frac{d\bar{C}_G}{dZ} + \frac{dA_G}{dZ} \bar{C}_G = \text{Pe}_G^{-1} \frac{d^2 \bar{C}_G}{dZ^2} - \bar{K}_G (\bar{C}_G - \bar{C}_L);$$

$$Z = 0, \quad \bar{C}_G = 1, \quad \frac{d\bar{C}_G}{dZ} = 0;$$

$$A_L \frac{d\bar{C}_L}{dZ} + \frac{dA_L}{dZ} \bar{C}_L = \text{Pe}_L^{-1} \frac{d^2 \bar{C}_L}{dZ^2} + \bar{K}_L (\bar{C}_G - \bar{C}_L);$$

$$Z = 0, \quad \bar{C}_L = 1, \quad \frac{d\bar{C}_L}{dZ} = 0. \quad (15)$$

In the cases $0 = \text{Fo} \leq 10^{-2}$, $0 = \text{Pe}^{-1} = \text{Fo} r_0^2 / l^2 \leq 10^{-2}$, $r_0^2 / l^2 < 1$ (see (5)) the model (15) has the convective form:

$$A_G \frac{d\bar{C}_G}{dZ} + \frac{dA_G}{dZ} \bar{C}_G = -\bar{K}_G (\bar{C}_G - \bar{C}_L); \quad Z = 0, \quad \bar{C}_G = 1;$$

$$A_L \frac{d\bar{C}_L}{dZ} + \frac{dA_L}{dZ} \bar{C}_L = \bar{K}_L (\bar{C}_G - \bar{C}_L); \quad Z = 0, \quad \bar{C}_L = 1. \quad (16)$$

The functions $A_G(Z)$ and $A_L(Z)$ (see (13), (14)) represent the effects of the velocities nonuniformities and is possible to be replaced [16] by linear approximations:

$$A_G = 1 + a_G Z, \quad A_L = 1 + a_L Z, \quad (17)$$

where the parameters a_G , a_L must be calculated [16], [17] as a solution of the inverse problem [13], using experimental data for $\bar{C}_G(Z)$ and $\bar{C}_L(Z)$, obtained on the column with real diameter and small high ($Z = 0.1$).

2. Chemical absorption

The increase of the absorption rate J [$\text{kg}\cdot\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] leads to the apparatuses size decrease. This rate is proportional to the concentration difference $c_G - c_G^*$, where c_G [$\text{kg}\cdot\text{mol}\cdot\text{m}^{-3}$] is SO_2 concentration in the gas volume and c_G^* [$\text{kg}\cdot\text{mol}\cdot\text{m}^{-3}$] is SO_2

concentration in the gas phase at the gas-liquid interphase [13]. A maximal absorption rate is possible if $c_G^* = 0$, i.e. in the cases of very fast irreversible chemical reactions of SO_2 in liquid phase, i.e. if highly concentrated alkaline absorbents are used.

The irreversible chemical reactions in the liquid phase, using alkaline absorbents (for example solutions of Na_2CO_3) affect significantly the gas-liquid interphase mass transfer. 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 [13].

2.1. Convection-diffusion type of model

Let's consider a chemical absorption, when the concentration of the reagent in the liquid phase is very big. In this case the mathematical model of the chemical absorption in a column apparatus in cylindrical coordinate system (z, r) , in the approximations of the mechanics of continua [13], has the form:

$$\omega_G u_G \frac{\partial c_G}{\partial z} = \omega_G D_G \left(\frac{\partial^2 c_G}{\partial z^2} + \frac{1}{r} \frac{\partial c_G}{\partial r} + \frac{\partial^2 c_G}{\partial r^2} \right) - k(c_G - \chi c_L),$$

$$\omega_L u_L \frac{\partial c_L}{\partial z} = \omega_L D_L \left(\frac{\partial^2 c_L}{\partial z^2} + \frac{1}{r} \frac{\partial c_L}{\partial r} + \frac{\partial^2 c_L}{\partial r^2} \right) + k(c_G - \chi c_L) - k_0 c_L, \quad (18)$$

where as boundary conditions is possible to be used (2).

The using of dimensionless (generalized) variables (3) and (5) leads to:

$$U_G \frac{\partial C_G}{\partial Z} = \text{Fo}_G \left(\varepsilon \frac{\partial^2 C_G}{\partial Z^2} + \frac{1}{R} \frac{\partial C_G}{\partial R} + \frac{\partial^2 C_G}{\partial R^2} \right) - \rho_G (C_G - C_L),$$

$$U_L \frac{\partial C_L}{\partial Z} = \text{Fo}_L \left(\varepsilon \frac{\partial^2 C_L}{\partial Z^2} + \frac{1}{R} \frac{\partial C_L}{\partial R} + \frac{\partial^2 C_L}{\partial R^2} \right) + \rho_L (C_G - C_L) - \text{Da}_L C_L; \quad (19)$$

$$Z = 0, \quad C_G(0, R) \equiv 1, \quad 1 \equiv U_G(R) - \text{Pe}_G^{-1} \left(\frac{\partial C_G}{\partial Z} \right)_{Z=0};$$

$$Z = 0, \quad C_L(0, R) \equiv 0, \quad 1 \equiv U_L(R) - \text{Pe}_L^{-1} \left(\frac{\partial C_L}{\partial Z} \right)_{Z=0};$$

$$R = 0, \quad \frac{\partial C_G}{\partial R} = \frac{\partial C_L}{\partial R} \equiv 0; \quad R = 1, \quad \frac{\partial C_G}{\partial R} = \frac{\partial C_L}{\partial R} \equiv 0;$$

where Da_L is the Damkohler number:

$$\text{Da}_L = \frac{k_0 l}{\omega_L u_L^0}. \quad (20)$$

In the cases $10^{-2} < \text{Da}_L < 1$ as dimensionless mass transfer resistances in the gas (ρ_G) and liquid (ρ_L) phases is possible to be used (6) and if $\phi \rightarrow \infty$, $\rho_G = 0$, $C_G \equiv 1$, the interphase mass

transfer is limited by the mass transfer in the liquid phase, while in the opposite case ($\phi=0, \rho_L=0, C_L \equiv 0$) the interphase mass transfer is limited by the mass transfer in the gas phase.

In the cases, where the chemical reaction has a considerable influence on the mass transfer in the column ($Da_L > 1$), the second equation in (19) has the form:

$$Da_L^{-1} U_L \frac{\partial C_L}{\partial Z} = \frac{Fo_L}{Da_L} \left(\varepsilon \frac{\partial^2 C_L}{\partial Z^2} + \frac{1}{R} \frac{\partial C_L}{\partial R} + \frac{\partial^2 C_L}{\partial R^2} \right) + \frac{\rho_L}{Da_L} (C_G - C_L) - C_L. \quad (21)$$

As dimensionless mass transfer resistances in the gas ($\hat{\rho}_G$) and liquid ($\hat{\rho}_L$) phases is possible to be used

$$\hat{\rho}_G = \frac{1}{1+\hat{\phi}}, \quad \hat{\rho}_L = \frac{\rho_L}{Da} = \frac{\hat{\phi}}{1+\hat{\phi}}, \quad \hat{\phi} = \frac{\omega_G u_G^0 \chi}{\omega_L u_L^0 Da} \quad (22)$$

and if $\hat{\phi} \rightarrow \infty, \hat{\rho}_G = 0, C_G \equiv 1$, the interphase mass transfer is limited by the mass transfer in the liquid phase, while in the opposite case ($\hat{\phi}=0, \hat{\rho}_L=0, C_L \equiv 0$) the interphase mass transfer is limited by the mass transfer in the gas phase.

The result obtained (22) allows the finding of optimal conditions for the absorption processes realization, i.e. the using of gas-liquid drops ($\hat{\phi}=0, \hat{\rho}_L=0, C_L \equiv 0$) or liquid-gas bubbles ($\hat{\phi} \rightarrow \infty, \rho_G=0, C_G \equiv 1$) systems. In (19) is possible to be used the approximations $0 = \varepsilon \leq 10^{-2}$ (see (7)) or $0 = Fo_G \leq 10^{-2}$ and $0 = Fo_L \leq 10^{-2}$ (see (8)).

2.2. Average concentration model

The use of the convection-diffusion type of models (19) for a quantitative description of the chemical absorption in column apparatuses is not possible because the velocity functions in the convection-diffusion equations are unknown. The average values of the velocity and concentration (9) over the cross-sectional area of the column must be used for to be obtained the average concentration model (by analogy of (12)):

$$\alpha_G \frac{d\bar{c}_G}{dz} + \frac{d\alpha_G}{dz} \bar{c}_G = \frac{D_G}{\bar{u}_G} \frac{d^2 \bar{c}_G}{dz^2} - \frac{k}{\omega_G \bar{u}_G} (\bar{c}_G - \chi \bar{c}_L);$$

$$z=0, \quad \bar{c}_G(0) = c_G^0, \quad \frac{d\bar{c}_G}{dz} = 0.$$

$$\alpha_L \frac{d\bar{c}_L}{dz} + \frac{d\alpha_L}{dz} \bar{c}_L = \frac{D_L}{\bar{u}_L} \frac{d^2 \bar{c}_L}{dz^2} + \frac{k}{\omega_L \bar{u}_L} (\bar{c}_G - \chi \bar{c}_L) - \frac{k_0}{\omega_L \bar{u}_L} \bar{c}_L;$$

$$z=0, \quad \bar{c}_L(0) = 0, \quad \frac{d\bar{c}_L}{dz} = 0. \quad (23)$$

The using of the generalized variables (14) leads to:

$$A_G \frac{d\bar{C}_G}{dZ} + \frac{dA_G}{dZ} \bar{C}_G = Pe_G^{-1} \frac{d^2 \bar{C}_G}{dZ^2} - \bar{K}_G (\bar{C}_G - \bar{C}_L);$$

$$Z=0, \quad \bar{C}_G = 1, \quad \frac{d\bar{C}_G}{dZ} = 0.$$

$$A_L \frac{d\bar{C}_L}{dZ} + \frac{dA_L}{dZ} \bar{C}_L = Pe_L^{-1} \frac{d^2 \bar{C}_L}{dZ^2} + \bar{K}_L (\bar{C}_G - \bar{C}_L) - Da_L \bar{C}_L;$$

$$Z=0, \quad \bar{C}_L = 1, \quad \frac{d\bar{C}_L}{dZ} = 0. \quad (24)$$

In the cases $0 = Fo \leq 10^{-2}, 0 = Pe^{-1} = Fo r_0^2 / l^2 \leq 10^{-2}, r_0^2 / l^2 < 1$ the model (24) has the convective form:

$$A_G \frac{d\bar{C}_G}{dZ} + \frac{dA_G}{dZ} \bar{C}_G = -\bar{K}_G (\bar{C}_G - \bar{C}_L);$$

$$Z=0, \quad \bar{C}_G = 1.$$

$$A_L \frac{d\bar{C}_L}{dZ} + \frac{dA_L}{dZ} \bar{C}_L = \bar{K}_L (\bar{C}_G - \bar{C}_L) - Da_L \bar{C}_L;$$

$$Z=0, \quad \bar{C}_L = 1. \quad (25)$$

The functions $A_G(Z)$ and $A_L(Z)$ (see (13), (14)) represent the effects of the velocities non-uniformities and is possible to be obtained by analogy of (17).

3. Two-phases absorbent method

In many practical cases are used two phases absorbents [18-20] (as water suspensions of $CaCO_3$ or $Ca(OH)_2$) because they have a low price and a big absorption capacity. The presence of the active component in the absorbent, as a solution and solid phase, leads to the introduction of a new process (the dissolution of the solid phase) and to creates conditions for variations of the absorption mechanism (interphase mass transfer through two interphase surfaces – gas/liquid and liquid/solid) [18-20].

Many companies (Babcock & Wilcox Power Generation Group, Inc., Alstom Power Italy, Idreco-Insigma-Consortium) provide methods and apparatuses for waste gases purification from SO_2 , using two-phase absorbent ($CaCO_3/H_2O$ suspension). 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 SO_2 absorption with two-phase absorbent will be presented, using the convection-diffusion model approximation.

3.1. Convection-diffusion type of model approximation

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 the dissolved $CaCO_3$ in the absorbent, the mass sources (sinks) 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 (equilibrium) solubility of CaCO_3 in water. As a result the convection-diffusion equations in a column apparatus for counter-current absorption process will be presented in two systems with cylindrical coordinates - (z_1, r) , (z_2, r) , $(z_1 + z_2 = l)$:

$$\begin{aligned} \varepsilon_1 u_1 \frac{\partial c_1}{\partial z_1} &= \varepsilon_1 D_1 \left(\frac{\partial^2 c_1}{\partial z_1^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial r^2} \right) - k(c_1 - \chi c_2), \\ \varepsilon_2 u_2 \frac{\partial c_2}{\partial z_2} &= \varepsilon_2 D_2 \left(\frac{\partial^2 c_2}{\partial z_2^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} + \frac{\partial^2 c_2}{\partial r^2} \right) + k(c_1 - \chi c_2) - k_0 c_2 c_3, \\ \varepsilon_2 u_2 \frac{\partial c_3}{\partial z_2} &= \varepsilon_2 D_3 \left(\frac{\partial^2 c_3}{\partial z_2^2} + \frac{1}{r} \frac{\partial c_3}{\partial r} + \frac{\partial^2 c_3}{\partial r^2} \right) - k_0 c_2 c_3 + k_1 (c_3^0 - c_3), \end{aligned} \quad (26)$$

where $u_1(r)$, $u_2(r)$ are velocity distributions in the gas and liquid phases, $c_i(z_i, r)$ and D_i ($i = 1, 2, 3$; $z_3 = z_2$) are the concentration distributions and the diffusivities of SO_2 in the gas and liquid phases and of CaCO_3 in the liquid phase, k_0 - chemical reaction rate constant, k , k_1 - interphase mass transfer coefficients.

The boundary conditions of (26) in column with radius r_0 and working zone height l have the form:

$$\begin{aligned} z_1 = 0, \quad 0 \leq r \leq r_0, \quad c_1(0, r) &\equiv c_1^0, \\ u_1^0 c_1^0 &\equiv u_1(r) c_1^0 - D_1 \left(\frac{\partial c_1}{\partial z_1} \right)_{z_1=0}; \\ z_2 = 0, \quad 0 \leq r \leq r_0, \quad c_2(0, r) &\equiv c_2^0, \\ u_2^0 c_2^0 &\equiv u_2(r) c_2^0 - D_2 \left(\frac{\partial c_2}{\partial z_2} \right)_{z_2=0}; \\ z_2 = 0, \quad 0 \leq r \leq r_0, \quad c_3(0, r) &\equiv c_3^0, \\ u_2^0 c_3^0 &\equiv u_2(r) c_3^0 - D_3 \left(\frac{\partial c_3}{\partial z_2} \right)_{z_2=0}; \\ r = 0, \quad 0 \leq z \leq l, \quad \frac{\partial c_1}{\partial r} &= \frac{\partial c_2}{\partial r} = \frac{\partial c_3}{\partial r} \equiv 0; \\ r = r_0, \quad 0 \leq z \leq l, \quad \frac{\partial c_1}{\partial r} &= \frac{\partial c_2}{\partial r} = \frac{\partial c_3}{\partial r} \equiv 0; \end{aligned} \quad (27)$$

where u_i^0 , c_i^0 , $i = 1, 2$, are the input 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 , $c_2^0 = 0$ practically.

A qualitative analysis of the model (26) is possible to be made, using dimensionless (generalized) variables [13]:

$$\begin{aligned} R = \frac{r}{r_0}, \quad Z_1 = \frac{z_1}{l}, \quad Z_2 = \frac{z_2}{l}, \quad U_1 = \frac{u_1}{\bar{u}_1}, \\ U_2 = \frac{u_2}{\bar{u}_2}, \quad C_1 = \frac{c_1}{c_1^0}, \quad C_2 = \frac{c_2 \chi}{c_1^0}, \quad C_3 = \frac{c_3}{c_3^0}. \end{aligned} \quad (28)$$

If put (28) into (26), the model in generalized variables has the form:

$$\begin{aligned} U_1 \frac{\partial C_1}{\partial Z_1} &= \frac{D_1 l}{\bar{u}_1 r_0^2} \left(\frac{\partial^2 C_1}{\partial Z_1^2} + \frac{1}{R} \frac{\partial C_1}{\partial R} + \frac{\partial^2 C_1}{\partial R^2} \right) - \frac{kl}{\varepsilon_1 \bar{u}_1} (C_1 - C_2), \\ U_2 \frac{\partial C_2}{\partial Z_2} &= \frac{D_2 l}{\bar{u}_2 r_0^2} \left(\frac{\partial^2 C_2}{\partial Z_2^2} + \frac{1}{R} \frac{\partial C_2}{\partial R} + \frac{\partial^2 C_2}{\partial R^2} \right) + \\ &+ \frac{kl \chi}{\varepsilon_2 \bar{u}_2} (C_1 - C_2) - \frac{k_0 l c_3^0}{\varepsilon_2 \bar{u}_2} C_2 C_3, \\ U_2 \frac{\partial C_3}{\partial Z_2} &= \frac{D_3 l}{\bar{u}_2 r_0^2} \left(\frac{\partial^2 C_3}{\partial Z_2^2} + \frac{1}{R} \frac{\partial C_3}{\partial R} + \frac{\partial^2 C_3}{\partial R^2} \right) - \\ &- \frac{k_0 l c_1^0}{\varepsilon_2 \bar{u}_2 \chi} C_2 C_3 + \frac{k_1 l}{\varepsilon_2 \bar{u}_2} (1 - C_3), \end{aligned} \quad (29)$$

where dimensionless chemical kinetic parameters are:

$$K = \frac{k_0 l c_3^0}{\varepsilon_2 \bar{u}_2}, \quad K_1 = \frac{k_0 l c_1^0}{\varepsilon_2 \bar{u}_2 \chi}. \quad (30)$$

The low SO_2 concentration ($c_1^0 \ll 10^{-4}$ [kg-mol.m⁻³]) in the waste gases of the thermal power plants, the low concentration of the dissolved CaCO_3 in the absorbent ($c_3^0 \ll 10^{-4}$ [kg-mol.m⁻³]) and Henry's number value of $\text{SO}_2 / \text{H}_2\text{O}$ ($\chi \ll 10^{-2}$), lead to:

$$\frac{K}{K_1} = \frac{\chi c_3^0}{c_1^0} \ll 10^{-2}, \quad (31)$$

i.e. if mass transfer of the dissolved CaCO_3 in the absorbent is a result of the chemical reaction ($K_1 \ll 1$), the chemical reaction effect on the interphase mass transfer of SO_2 between the gas and liquid is possible to be neglected ($0 = K \ll 10^{-2}$). In these conditions the chemical reaction is very slow and as a result of the brief existence of the drops in the gas/liquid dispersion, the chemical reaction passes in the collected absorbent in the bottom half of the column.

The presented theoretical analysis shows, that in the cases of waste gases purification from SO_2 , using two-phase absorbent ($\text{CaCO}_3/\text{H}_2\text{O}$ suspension), the interphase mass transfer process in the system gas-liquid drops is practically physical absorption as a result of the low concentration of the dissolved SO_2 and CaCO_3 in the water and the mathematical model is possible to be obtained directly from the model (1), (2), where $c_2^0 = 0$:

$$\begin{aligned} \varepsilon_1 u_1 \frac{\partial c_1}{\partial z_1} &= \varepsilon_1 D_1 \left(\frac{\partial^2 c_1}{\partial z_1^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial r^2} \right) - k(c_1 - \chi c_2), \\ \varepsilon_2 u_2 \frac{\partial c_2}{\partial z_2} &= \varepsilon_2 D_2 \left(\frac{\partial^2 c_2}{\partial z_2^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} + \frac{\partial^2 c_2}{\partial r^2} \right) + k(c_1 - \chi c_2); \\ z_1 = 0, \quad c_1(0, r) &\equiv c_1^0, \quad \bar{u}_1 c_1^0 \equiv u_1(r) c_1^0 - D_1 \left(\frac{\partial c_1}{\partial z_1} \right)_{z_1=0}; \quad (32) \\ z_2 = 0, \quad c_2(0, r) &\equiv 0, \quad \left(\frac{\partial c_2}{\partial z_2} \right)_{z_2=0} \equiv 0; \\ r = 0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_1}{\partial r} = \frac{\partial c_2}{\partial r} \equiv 0. \end{aligned}$$

The theoretical analysis of this model (see (4), (5), (6)) shows, that 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 realized in a new method and apparatus for gas absorption [21] in a two-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 lower 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 this 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. In the column tank, the chemical reaction takes place, only.

Conclusion

A theoretical analysis of sulfur dioxide removal from the waste gases in thermal power plants is presented. A new approach (on the base of the approximations of the mechanics of continua) for modeling of the absorption processes in column apparatuses is used. The proposed convection-diffusion type of models for a qualitative analysis the mechanism and kinetics of the gas absorption in column apparatuses is used for to be obtained the mass transfer resistances in the gas and liquid phases. On this base is possible to be obtained the limiting phase (phase with the higher mass transfer resistance) and optimal gas-liquid system for gas absorption (gas-liquid drops system if the limiting phase is the gas and liquid-gas bubbles system in the opposite case).

The theoretical analysis of the methods and apparatuses for waste gases purification from SO_2 , using two-phase absorbent (CaCO_3 suspension) shows, that the process is physical absorption practically and the mass transfer resistances in the gas and liquid phases are 44% and 56% respectively. In these conditions a process optimization is possible in two-zone column, where

the upper zone is physical absorption in gas-liquid drops system and the lower zone is chemical absorption in liquid-gas bubbles system. The chemical reaction takes place in the column tank.

The convection-diffusion type of models permits to be created the average concentration models and to be made quantitative description of the absorption processes.

References

- i. Boyadjiev, Chr., *On the Purification of Gases containing Impurities of small Concentrations*. Hungarian J. Ind. Chem., 2002, vol. 30, p.103.
- ii. Boyadjiev, Chr., *On the SO_2 problem in power engineering*, Proceedings of Energy Forum, Varna, Bulgaria, 2011, p. 114.
- iii. Boyadjiev, Chr. *On the SO_2 problem in power engineering*, Proceedings of Asia-Pacific Power and Energy Engineering Conference (APPEEC 2012), Shanghai, China, 2012. vol. 1
- iv. Boyadjiev, Chr., Doichinova, M., Popova, P., *On the SO_2 problem in power engineering*, Transactions of Academenergo, 2012, no. 1, p. 44.
- v. Ramm, V.M., *Gas Absorption*, Khimia, Moscow, 1966 (in Russian).
- vi. Danckwerts, P.V., *Gas-Liquid Reactions*, McGraw-Hill, New York, 1970.
- vii. Lewis, W.K., Whitman, W.G., *Ind. Eng. Chem.*, 1924, vol. 16, p.1215.
- viii. Higbie, R., *Trans. Am. Inst. Chem. Eng.*, 1935, vol. 31, p.365.
- ix. Kishinevsky, M.Kh., Pamfilov, A.V., *J. Appl. Chem. (Russia)*, 1949, vol. 22, p.1173.
- x. Kishinevsky, M.Kh., *J. Appl. Chem. (Russia)*, 1951, vol. 24 p.542.
- xi. Danckwerts, P.V., *Ind. Eng. Chem.*, 1951, vol. 43, p.1960.
- xii. Levich, V.G., *Physicochemical Hydrodynamics*, Prentice Hall, New York, 1962.
- xiii. Boyadjiev, Chr., *Theoretical Chemical Engineering. Modeling and simulation*, Springer-Verlag, Berlin Heidelberg, 2010.
- xiv. Boyadjiev Chr., *Diffusion models and scale-up*, Int. J. Heat Mass Transfer, 2006, vol. 49, p. 796.
- xv. Boyadjiev, Chr., *Modeling of column apparatuses*, Transactions of Academenergo, 2009, no. 3, p. 7.
- xvi. Doichinova, M., Boyadjiev, Chr., *On the column apparatuses modeling*, Int. J. Heat Mass Transfer, 2012, vol. 55, p. 6705.
- xvii. Boyadjiev, Chr., *A new approach for the column apparatuses modeling in chemical engineering*, J. Appl. Math.:Advances and Applications, 2013, vol. 10, no. 2, p.131.
- xviii. Boyadjiev, Chr., *Mechanism of gas absorption with two-phase absorbents*, International Journal of Heat and Mass Transfer, 2011, vol. 54, p. 3004.
- xix. Boyadjiev, Chr., Doichinova, M., Popova, P., *On the SO_2 Problem in Power Engineering.1. Gas absorption*, Proceedings of 15th Workshop on Transport Phenomena in Two-Phase Flow, Sunny Beach Resort, Bulgaria, 2011, p. 94.
- xx. Boyadjiev, Chr., Popova, P., Doichinova, M., *On the SO_2 problem in power engineering. 2. Two-phase absorbents*, Proceedings of 15th Workshop on Transport Phenomena in Two-Phase Flow, Sunny Beach Resort, Bulgaria, 2011, p. 104.
- xxi. Boyadjiev, Chr., Boyadjiev, B., Doichinova, M., Popova-Krumova, P., *Method and apparatus for gas absorption*, Bulgarian Patent 111168, 2013.