

Mathematical Modeling of Absorption-adsorption Processes for Waste Free Decontamination of Gases from SO₂ in a Bubble Tray Column

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Abstract. Integrated absorption-adsorption for waste free desulfurization of gases from SO₂ in a bubble tray column is presented. The method includes physical absorption of SO₂ with water and chemical adsorption of HSO₃⁻ from the water solution by particles anionite. The two steps method is integrated in one apparatus-a bubble tray column. This method is regenerative and the regeneration is made with solution of ammonium hydroxide. The further step for utilization of the obtained (NH₄)₂SO₃ and (NH₄HSO₃) is by using HNO₃ for production of concentrated SO₂ (gas) and NH₄NO₃ (solution). Convection-diffusion and average concentration models are presented, which are used to describe absorption and adsorption processes. A comparison of the calculated trough the mathematical model and the experimental data is shown.

1 Introduction

Sulphur dioxide is an acid greenhouse gas and the efforts to eliminate it are in the focus of the scientific interest for many years. Cost-effective methods for obtaining valuable products are the main goal to reduce it.

The most used apparatuses up to now use absorption in a CaCO₃ suspension (Wilcox Power Generation Group and Babcock Inc., Italy, Idreco-Insigma-Consortium). This method has the shortcoming of generating new wastes and their disposal [1–3]. Another disadvantage here is that the absorption of sulphur dioxide releases CO₂ in the atmosphere that is a greenhouse gas also. Another disadvantage of this method is that it is nonregenerable one and uses large quantities of natural carbonates.

The process in the column in the flow of gas-liquid drops is practically physical absorption as a result of the small concentration of dissolved CaCO₃ and SO₂ in the drops and its short existence in the gas-liquid dispersion, which is proven by the theoretical analysis of the gas purification method and apparatus from SO₂ with a two-phase absorbent (CaCO₃ suspension) [4–14].

A proposed patent [15], eliminates these disadvantages by dividing of the absorption column in two zones - lower zone (liquid-gas bubbles) and upper zone (gas-liquid drops). This leads to increasing the degree of absorption process and lowers the apparatus height.

In this case, anionites (anion-exchange resins -R-OH form of Varion, Duolite, Wofatit, Kastel, Amberlite) as adsorbents [16–18] are used and the process is regenerable. The expression for the chemical reaction of SO₂ has the form:



The regeneration can be presented as:



In the described method [19], the adsorption takes place in the gas phase, and the adsorbent regeneration in the liquid phase. AmberLite® FPA66 (Dowex® 66) was selected as the most suitable for the realization of the process, as shown in our previous study [20].

2 Absorption-adsorption approach

Regeneration of the adsorbent is carried out with an ammonium hydroxide solution (see (2)). In order to obtain valuable product the (NH₄)₂SO₃ obtained is treated with nitric acid and concentrated SO₂ is received together with ammonium nitrate as fertilizer.

This method for waste gas cleaning from SO₂ is possible to be realized in two variants:

1. Two apparatuses method: The first apparatus is a co-current column, where the process is physical stationary absorption of SO₂ in water. The water from the outlet of the first column enters the second column, where it passes through a fixed layer of synthetic anion exchange resin particles [21].
2. One apparatus method (tray column). Both processes are conducted simultaneously in a water anionite suspension.

2.1 One Apparatus Method

The absorption-adsorption method for waste gas cleaning from SO₂ is possible to be realized in one column, where the synthetic anionite particles are as water suspension. The gas enters in the column, SO₂ is absorbed from the water and adsorbed from the synthetic anionite particles. The adsorbent is saturated gradually and as a result, the process is non-stationary.

2.1.1 Absorption – adsorption modeling

The modeling of the processes in this column use the next convection-diffusion model [22–24]:

$$\begin{aligned} u \frac{\partial c_{11}}{\partial z} &= D_1 \left(\frac{\partial^2 c_{11}}{\partial z^2} + \frac{1}{r} \frac{\partial c_{11}}{\partial r} + \frac{\partial^2 c_{11}}{\partial r^2} \right) - k(c_{11} - \chi c_{12}); \\ \frac{dc_{13}}{dt} &= k(c_{12} - c_{13}) - k_1 c_{13} c_{23} = 0; \quad \frac{dc_{23}}{dt} = -k_1 c_{13} c_{23}; \\ t = 0, \quad c_{11} &\equiv c_{11}^0, \quad c_{13} \equiv 0, \quad c_{23} \equiv c_{23}^0; \\ r = 0, \quad \frac{\partial c_{11}}{\partial r} &\equiv 0; \quad r = r_0, \quad \frac{\partial c_{11}}{\partial r} \equiv 0; \\ z = 0, \quad c_{11} &\equiv c_{11}^0, \quad \frac{\partial c_{11}}{\partial z} \equiv 0. \end{aligned} \quad (3)$$

In the model (3) u , c_{11} , D_1 are the velocity, concentration and diffusion coefficient of sulphur dioxide in the gas, c_{13} – the SO₂ concentration in the adsorbent, c_{23} is the active sides in the adsorbent, c_{11}^0 - inlet SO₂ concentration in the gas, c_{23}^0 – initial concentration of the active sides.

2.1.2 Tray column method

The gas passes through a layer of water suspension of synthetic anionite in the apparatus with bubbling trays [25, 26]. The increased gas velocity in this case leads to a reduction of the column diameter. As it is known, the absorption of sulphur dioxide is limited by mass transfer in the gas phase, and the absorption rate is intensified additionally due to its mixing in the gas while passing between the trays.

- A scheme of the bubble tray apparatus [25, 26] is given in Fig. 1.
- The following cyclic scheme is used for the opperation of the buble tray column:
- A. The plates are loaded with a certain amount (volume) of suspension of synthetic anionite.
 - B. After starting, the process and the SO₂ concentration is monitored at the exit 3 of the column 1.
 - C. When the concentration of SO₂ at the gas outlet 3 exceeds preliminary preset limits, the suspension from the bottom tray is transferred in the regeneration system 9 and the tray is supplied with already regenerated anionite.
 - D. Then the procedure is repeated for the second, third etc.

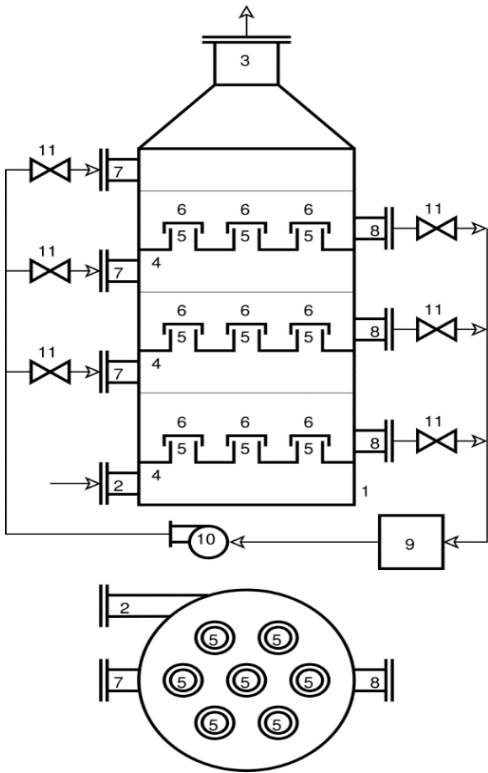


Fig. 1. Tray column method (1-column, 2-inlet, 3- outlet, 4-plates, 5-distribution pipes, 6-concentric bubble caps, 7, 8- pipes, 9- regeneration system, 10- pump, 11- valves)

3 Experimental set-up

A photo of the realized experimental installation is given in Fig. 2. The installation is with one tray and a single bubble-cap.

Kinetics studies in the constructed installation were conducted at flow rate of 15000 l/h and two concentrations of sulfur dioxide (1500 ppm and 3600 ppm 0.015% to 0.36%). Sulfur dioxide concentrations at the inlet and outlet of the installation were determined using a portable gas analyzer Optima 7, and in the liquid phase by iodometric titration. The concentration of sulfur dioxide is additionally adjusted with a rotameter. The quantity of the water was 4.5 l and the quantity of the anionite was 500 g.



Fig. 2. Experimental installation with a single tray and on bubble-cap.

4 Absorption-adsorption Process Modeling

The absorption-adsorption in the column is two component ($i = 1, 2$ for the SO_2 and synthetic anionite, respectively) and three phase ($j = 1, 2, 3$ for the gas, liquid and solid phases, respectively) process, where $u_j, c_{ij}(t, z)$ are the velocities and concentrations, t is the time, z is the axial coordinate.

The tangential gas feed into the column reduces the radial non-uniformity in the cross-sectional area of the column and thereby increases the mass transfer rate. In addition, the gas creates a regime of ideal mixing in the liquid phase and the concentration of SO_2 in the liquid phase is $c_{12} = c_{12}(t)$.

A combination of physical absorption and chemical adsorption models is used to describing the non-stationary absorption-adsorption process for purification of gases from SO₂ [25, 26] on the plate number n ($n = 1, \dots, N$).

$$\begin{aligned} \frac{\partial c_{11}^{(n)}}{\partial t} + u_1 \frac{\partial c_{11}^{(n)}}{\partial z} &= D_1 \frac{\partial^2 c_{11}^{(n)}}{\partial z^2} - k_0 (c_{11}^{(n)} - \chi c_{12}^{(n)}); \\ \frac{\partial c_{12}^{(n)}}{\partial t} + u_1 \frac{\partial c_{12}^{(n)}}{\partial z} &= D_1 \frac{\partial^2 c_{12}^{(n)}}{\partial z^2} + k_0 (c_{11}^{(n)} - \chi c_{12}^{(n)}) - k_1 (c_{12}^{(n)} - c_{13}^{(n)}); \\ \frac{dc_{13}^{(n)}}{dt} &= k_1 (c_{12}^{(n)} - c_{13}^{(n)}) - k c_{13}^{(n)} c_{23}^{(n)}; \quad \frac{dc_{23}^{(n)}}{dt} = -k c_{13}^{(n)} c_{23}^{(n)}; \\ t = 0, \quad c_{11}^{(n)} &\equiv c_{11}^0, \quad c_{12}^{(n)} \equiv 0, \quad c_{13}^{(n)} \equiv 0, \quad c_{23}^{(n)} \equiv c_{23}^0; \\ z = 0, \quad c_{11}^{(n)}(0) &\equiv c_{11}^{(n-1)}(l), \quad 0 \equiv \left(\frac{\partial c_{11}^{(n)}}{\partial z} \right)_{z=0}, \quad c_{11}^{(1)}(0) \equiv c_{11}^0, \quad 0 \equiv \left(\frac{\partial c_{12}^{(n)}}{\partial z} \right)_{z=0} \\ z = l, \quad 0 &\equiv \left(\frac{\partial c_{12}^{(n)}}{\partial z} \right)_{z=l}. \end{aligned} \quad (4)$$

In (4) $z = 0$ is the inlet of the gas on the tray number n ($n = 1, \dots, N$), l [m] is the space between the plates, k_0, k_1 – interphase mass transfer coefficients, k – chemical reaction rate constant.

The concentration of SO₂ in the liquid on each plate is obtained by the equality of absorption V_1 and adsorption V_2 rates:

$$V_1 = Q [c_{11}^{(n)}(0) - c_{11}^{(n)}(l)], V_2 = W [k_1 (c_{12}^{(n)} - c_{13}^{(n)}) - k c_{13}^{(n)} c_{23}^{(n)}], \quad (5)$$

where Q is the gas flow rate, W – solid phase volume. As a result:

$$c_{12}^{(n)} = \frac{Q [c_{11}^{(n)}(0) - c_{11}^{(n)}(l)]}{W k_1} + c_{23}^{(n)} \left[\frac{k}{k_1} c_{13}^{(n)} + 1 \right]. \quad (6)$$

Experimental installation with a single tray and bubble cap is constructed and experiments for determination of the inlet and outlet concentrations of the gas phase and the liquid phase as a function of time were carried out. Additionally an apparatus with two trays will be constructed and experiments with different initial concentrations and velocities of the gas phase will be conducted.

The experimental data are used to identify the parameters in the mathematical model of the integrated absorption – adsorption approach, proposed in this study. The mathematical description of the physical absorption and chemical adsorption models in a single tray and bubble cap in dimensionless form can be expressed:

$$\begin{aligned} \gamma \frac{\partial C_{11}^{(n)}}{\partial T} + U_1 \frac{\partial C_{11}^{(n)}}{\partial Z} &= Pe^{-1} \frac{\partial^2 C_{11}^{(n)}}{\partial Z^2} - K_0 (C_{11}^{(n)} - C_{12}^{(n)}), \\ \gamma \frac{\partial C_{12}^{(n)}}{\partial T} + U_1 \frac{\partial C_{12}^{(n)}}{\partial Z} &= Pe^{-1} \frac{\partial^2 C_{12}^{(n)}}{\partial Z^2} + K_0 (C_{11}^{(n)} - C_{12}^{(n)}) - K_1 (C_{12}^{(n)} - C_{13}^{(n)}), \\ \frac{dC_{13}^{(n)}}{dT} &= K_1 (C_{12}^{(n)} - C_{13}^{(n)}) - K C_{13}^{(n)} C_{23}^{(n)}, \\ \frac{dC_{23}^{(n)}}{dT} &= -K_2 C_{13}^{(n)} C_{23}^{(n)}, \end{aligned} \quad (7)$$

$$T=0, \quad C_{11}^{(n)} \equiv C_{11}^0, \quad C_{12}^{(n)} \equiv 0, \quad C_{13}^{(n)} \equiv 0, \quad C_{23}^{(n)} \equiv C_{23}^0;$$

$$Z=0, \quad C_{11}^{(n)}(0) = C_{11}^{(n-1)}(1), \quad \left(\frac{\partial C_{11}^{(n)}}{\partial Z} \right)_{Z=0} \equiv 0, \quad C_{11}^{(1)}(0) = C_{11}^0, \quad C_{12}^{(1)}(0) = 0, \quad \left(\frac{\partial C_{12}^{(n)}}{\partial Z} \right)_{Z=0} \equiv 0;$$

$$Z=1, \quad \left(\frac{\partial C_{12}^{(n)}}{\partial Z} \right)_{Z=1} \equiv 0; \quad n=1, \dots, N.$$

where

$$\begin{aligned} C_{11} &= \frac{c_{11}}{c_{11}^0}, \quad C_{12} = \frac{c_{12}\chi}{c_{11}^0}, \quad C_{13} = \frac{c_{13}\chi}{c_{11}^0}, \quad C_{23} = \frac{c_{23}}{c_{23}^0}, \\ T &= \frac{t}{t_0}, \quad Z = \frac{z}{l}, \quad U_1 = \frac{u_1}{u_1^0}, \quad \gamma = \frac{l}{t_0 u_1^0}, \quad Pe^{-1} = \frac{D_1}{u_1^0 l}, \\ K_0 &= \frac{k_0 l}{u_1^0}, \quad K_1 = k_1 t_0, \quad K = k c_{23}^0 t_0, \quad K_2 = \frac{k c_{11}^0 t_0}{\chi}, \end{aligned} \quad (8)$$

$$\chi = 3.21 \cdot 10^{-2}, \quad Q = 1.3889 \text{ l/s}, \quad W = 0.5 \text{ l},$$

$$u_1^0 = u_1 = 0.022 \text{ m/s}, \quad l = 0.153 \text{ m}, \quad c_{11}^0 = 0.0114 \text{ g/l}.$$

In the case when the experiments were carried out in a single tray column $n=1$.

The expression for concentration of SO_2 in the water has the form:

$$c_{12}^{(n)} = \frac{Q [c_{11}^{(n)}(0) - c_{11}^{(n)}(l)]}{W k_1} + c_{23}^{(n)} \left[\frac{k}{k_1} c_{13}^{(n)} + 1 \right]. \quad (9)$$

The experimental data are used to identify the parameters in the mathematical model of the integrated absorption –adsorption approach.

The model parameter values calculated by least square functions minimization are presented in Table 1:

$$Q_1(K_0, Pe, K, K_1, K_2) = \frac{1}{P} \sum_{i=1}^P (C_{11i} - C_{11i}^{\exp})^2 + \frac{1}{P} \sum_{i=1}^P (C_{12i} - C_{12i}^{\exp})^2 \rightarrow \min \quad (10)$$

where $i=1, \dots, P$ is the experimental data number.

Table 1. Model parameter values

$K [-]$	$K_0 [-]$	$K_1 [-]$	$K_2 [-]$	$Pe [-]$
1.0371	1.0251	0.9815	1.0313	0.9958

The comparison of the calculated values and experimental data for dimensionless concentration of SO₂ in the gas phase with different initial SO₂ concentration is presented in the Figs. 3, 4.

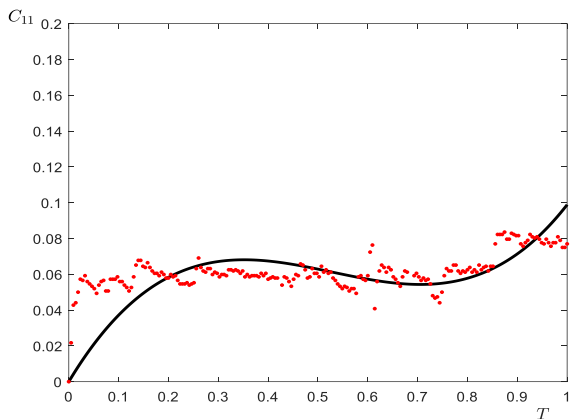


Fig. 3. Comparison of the calculated values and experimental data for dimensionless concentration of SO₂ in the gas phase (SO₂⁰=1500 ppm)

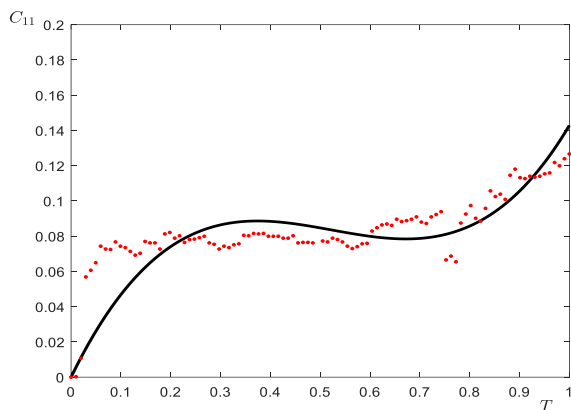


Fig. 4. Comparison of the calculated values and experimental data for dimensionless concentration of SO₂ in the gas phase (SO₂⁰=3600 ppm)

The obtained model results and their comparison with the experimental data for dimensionless concentration of SO₂ in the liquid phase with different initial concentration of SO₂ are presented in the Figs. 5, 6.

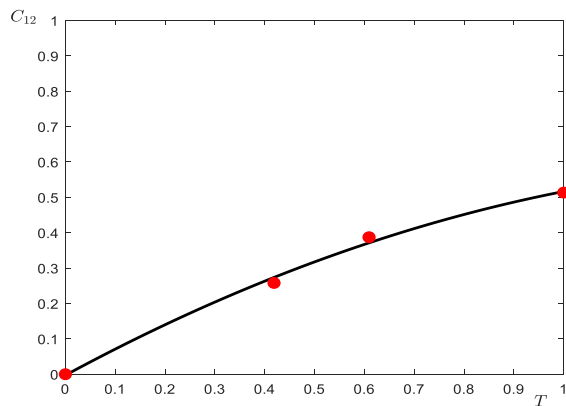


Fig. 5. Comparison of the calculated values and experimental data for dimensionless concentration of SO₂ in the water (SO₂⁰=1500 ppm)

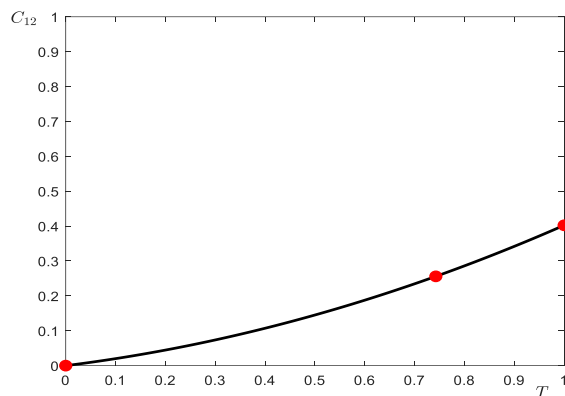


Fig. 6. Comparison of the calculated values and experimental data for dimensionless concentration of SO₂ in the water (SO₂⁰=3600 ppm)

5 Conclusion

The paper is devoted to a waste-free technology for desulfurization with regeneration. Average-concentration and convection-diffusion models of the absorption and adsorption processes allow modeling of the patented processes.

The obtained from the mathematical modeling results are in a good agreement with the experimental data in both cases-with initial concentrations of sulfur dioxide 1500 ppm and 3600 ppm, and 500 g. anionite AmberLite® FPA66 (Dowex® 66). From the results (Figs. 3, 4) it can be concluded that three zones were distinguished. In the first zone, the outlet concentration as a function of time increases rather steeply, after which a plateau is observed in the curve and another steep increase in concentration follows. This course of the curve is logical and can be explained by the adsorption of sulfur dioxide in water and it is adsorption in the ion exchange resin. The final sharp rise is interpreted by saturation of the liquid and the resin.

The future experimental results will help the successfully modelling, sizing of the tray columns and implementation of the new approach in the industry.

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