Absorption of SO$_2$ in the MgO–SO$_2$–H$_2$O and in the Ca^{2+}–SO$_2$–H$_2$O System

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In memory of Prof. Emeritus Vera Johanides

The engineering analysis of SO$_2$ absorption is presented in two different aqueous systems, corresponding to two industrial processes; in the MgO–SO$_2$–H$_2$O system (SO$_2$ absorption in the magnesium based pulp production) and in the Ca^{2+}–SO$_2$–H$_2$O system (limestone spray scrubbing process for absorbing SO$_2$ from the power plants).

A thermodynamic model used for constructing the equilibrium diagram for the both systems was developed. The diagrams present the relationship between the concentration of total SO$_2$, the concentration of combined SO$_2$, the concentration of true free SO$_2$ and the pH value. The overall processes in both systems were divided into three partial processes and their mass balances were graphically presented in the corresponding equilibrium diagram.

Equilibrium diagrams were proven to be useful tools for quantitative analysis (including equilibrium, mass balances, process kinetics) of SO$_2$ absorption in Mg^{2+} and Ca^{2+} based solutions. Results of the analysis of the both industrial cases are added.

Keywords:

Absorption of SO$_2$, equilibrium diagram, Pitzer ion-interaction model, mass transfer analysis

Introduction

The absorption of SO$_2$ is an important process in pulp production and also in the coal-fired power plants, where its role is the protection of environment. There has been considerable research work done in the field of the absorption of SO$_2$ into aqueous solutions. An early contribution dealing with the equilibrium in the MgO–SO$_2$–H$_2$O system is the work of *Hagefeldt*[1], showing the experimentally obtained equilibrium diagram, representing the concentrations of total SO$_2$, of combined SO$_2$, of true free SO$_2$ and the pH value of the solution. Important research study on the equilibrium in an electrolyte solution is the work of *Pasiuk-Bronikowska* and *Rudzinski*[2], who presented a method of modeling SO$_2$ absorption into aqueous solutions containing sulfites, based on the film theory of gas absorption and the chemical-equilibrium treatment of chemical reactions. Among others, a recent study[3], describing the industrial operation, has contributed to a better understanding of the pulp production and flue gas desulfurization. Several publications deal with the modeling of SO$_2$ absorption into calcium sulfite or limestone slurries[4–6], but the complexity of this system requires further intensive work in order to understand the process better.

In the present work the research study on the process in the MgO–SO$_2$–H$_2$O system – absorption of SO$_2$ in the industrial magnesium based paper pulp production – and in the Ca^{2+}–SO$_2$–H$_2$O system – industrial limestone spray scrubbing process for absorbing SO$_2$ emitting from the power plants – is presented.

In the work of *Zidar* et al.[7] the concentrations of total SO$_2$ (c_{tot}), of combined SO$_2$ (c_{com}), of true free SO$_2$ (Y) and the pH value of the solution were presented in the equilibrium diagram, it was constructed for the MgO–SO$_2$–H$_2$O system. The quantity Y is defined as the excess of SO$_2$ over the amount necessary to form Mg(HSO$_3$)$_2$ only, per unit mass of solution; c_{com} is the total concentration of Mg^{2+} in the solution, expressed with SO$_3^{2-}$ and HSO$_3^-$, using the corresponding stoichiometric factors, per unit mass of solution; and c$_{tot}$ is the amount of total SO$_2$, per unit mass of solution. These definitions of concentrations were taken for the MgO–SO$_2$–H$_2$O system[7], but for the Ca^{2+}–SO$_2$–H$_2$O system the molar concentrations[9] were used.

These relations are defined as follows:

$$Y = c_{tot} - 2c_{com} \tag{1}$$

$$c_{com} = c_{SO_3^{2-}} + 0.5\, c_{HSO_3^-} \tag{2}$$

$$c_{tot} = c_{SO_2} + c_{SO_3^{2-}} + c_{HSO_3^-} \qquad (3)$$

where c_{SO_2}, $c_{SO_3^{2-}}$, $c_{HSO_3^-}$ are the concentrations of the sulfur containing species present in the solution.
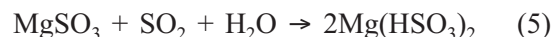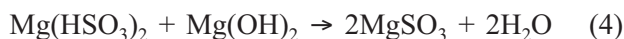
In the model developed for the construction of the diagram the relevant equilibrium reactions with the thermodynamic equilibrium constants for the SO$_2$–HSO$_3^-$–SO$_3^{2-}$–H$_2$O system, charge balance equation, mass balance equation and the modified Debye-Hückel equation for the computation of activity coefficients were used. Later in the study the latter was substituted with the Pitzer ion–interaction model. The calculated concentrations were in good agreement with the data measured by Hagefeldt[1].

Absorption of SO$_2$ in the MgO–SO$_2$–H$_2$O system (industrial magnesium based paper–pulp production)

The industrial plant (Fig. 1) for the absorbing of SO$_2$ emerging from the magnesium based paper–pulp production consists of four Venturi absorbers, a fortification tower to provide the contact between one part of the acid flowing out of the absorbers and sulfur dioxide from the sulfur burner, and a cooking acid storage tank, used to mix the enriched acid from the fortification tower and the other part of the acid from the absorbers, thus pro-

viding a required concentration of acid for the desulfurization process. Fresh Mg(OH)$_2$ is added on the each stage of the Venturi absorber.

The process of the absorption of SO$_2$ was divided into three partial processes; the mixing of flows, the reaction of the Mg(HSO$_3$)$_2$ with the Mg(OH)$_2$ added (reaction (4)) and the absorption of SO$_2$ (reaction of SO$_2$ with the MgSO$_3$, reaction (5))[7];

$$Mg(HSO_3)_2 + Mg(OH)_2 \rightarrow 2MgSO_3 + 2H_2O \qquad (4)$$

$$MgSO_3 + SO_2 + H_2O \rightarrow 2Mg(HSO_3)_2 \qquad (5)$$

The reaction (4) takes place at the constant concentration of total SO$_2$ and is represented by the slanting lines, while the reaction (5) occurs at the constant concentration of combined SO$_2$ and is represented by the vertical lines in the equilibrium diagram. To explain why the concentration of combined SO$_2$ remains constant during the partial process of the absorption of SO$_2$, expressions (6) and (7) are introduced into the equation (5)[7];

$$c_{SO_3^{2-},end} = c_{SO_3^{2-},start} - c_{SO_2} \qquad (6)$$

$$c_{HSO_3^-,end} = c_{HSO_3^-,start} + 2c_{SO_2} \qquad (7)$$

During the absorption process, the concentration of SO$_3^{2-}$ is equal to the difference between the initial concentration of SO$_3^{2-}$ and the concentration of SO$_2$, c_{SO2}, formed by the SO$_2$ absorption. The
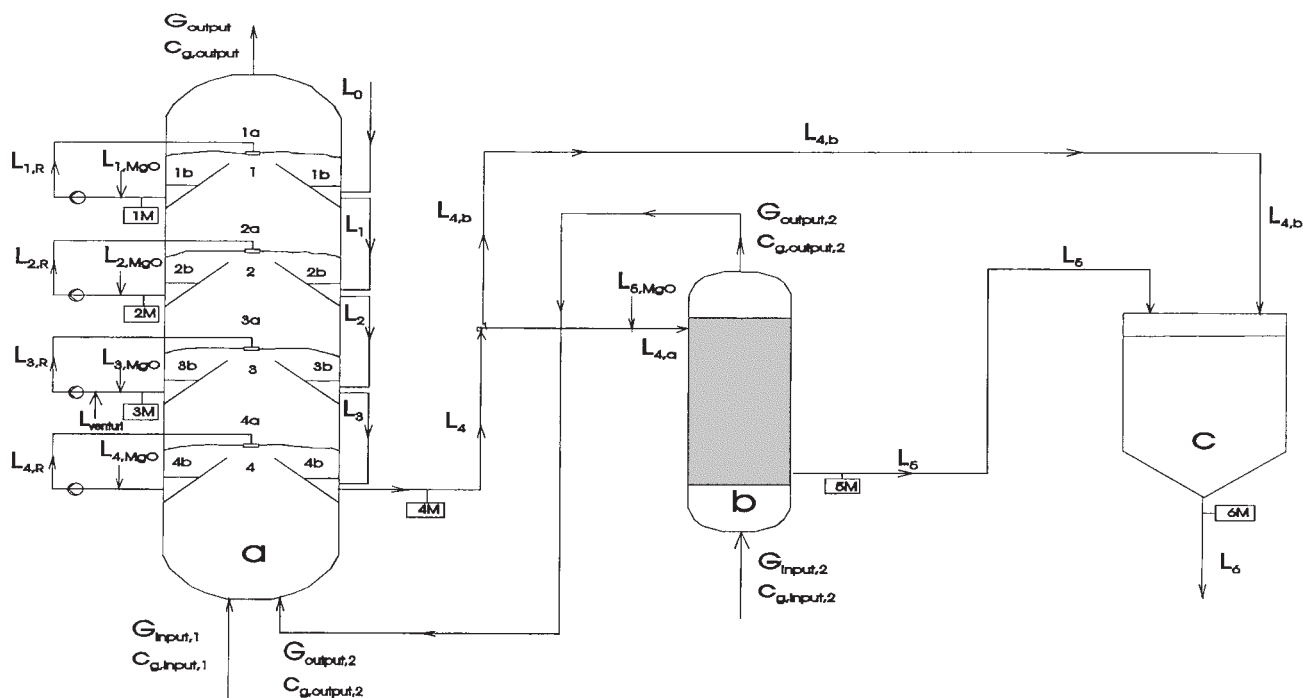

F i g . 1 – *Flow diagram of a commercial Venturi absorption system and of the fortification system of the magnesia pulping process (a, commercial four-Venturi absorption system; b, fortification tower; c, cooking acid storage tank; 1–4 – first, second, third, fourth commercial Venturi; 1a–4a – first, second, third, fourth spray; 1b–4b, first, second, third, fourth collection tanks; 1M–6M, measured sites for c_{tot}, c_{com}, and pH)*[7].
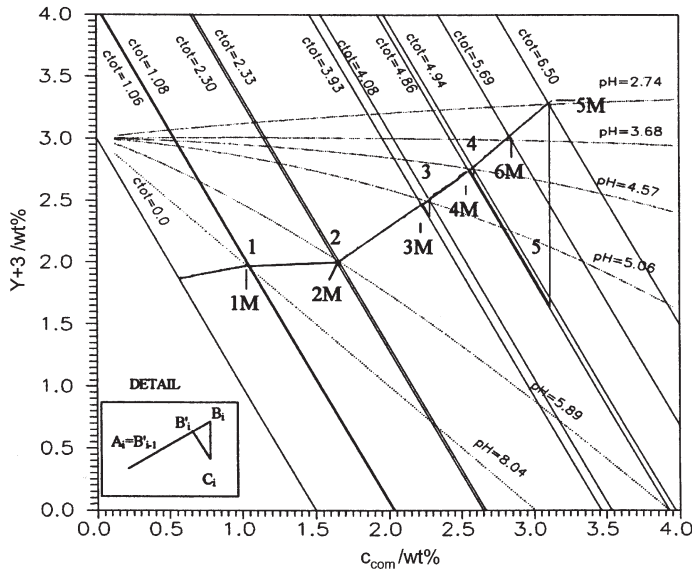
F i g . 2 – *Graphical presentation of the partial processes in the equilibrium diagram at 25°C, (1–5 – stages of the four Venturis and of the fortification tower with the acid cooking storage tank; 1M–6M – measured values of c_{tot}, c_{com}, pH value of each stage; DETAIL – represents the operation of each stage from 1 to 5, AB'B represents mixing, B'C reaction (4) and CB reaction (5)*[7].

concentration of HSO_3^- is equal to the sum of the initial concentration of HSO_3^- and the concentration of SO_2, $2c_{SO2}$, formed by the SO_2 absorption.

The partial processes were graphically presented in the equilibrium diagram (Fig. 2). The data used for the presentation of the industrial absorbing process were given in Table 1 of the work by *Zidar* et al.[7]

In the next publication by *Zidar* et al.[8] instead of the Debye-Hückel equation the Pitzer ion–interaction model for the computation of activity coefficients was used, which improved the theoretical description of the system and it also enabled calculating the isobaric curves for SO_2, the solubility curve for $MgSO_3$ and the construction of the equilibrium diagram at 50°C.

Absorption of SO₂ in the Ca²⁺–SO₂–H₂O system (industrial limestone spray scrubbing process)
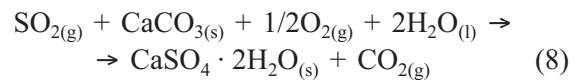
The constructing of the equilibrium diagram for the MgO–SO₂–H₂O system, which gave satisfying agreement with the measured data, enabled the constructing of the diagram for the Ca²⁺–SO₂–H₂O system using the analogous thermodynamic model. Clearly for this system the Pitzer parameters for the Ca-ion–interactions had to be used. The carbonate and sulfate species may also be of some importance in the Ca²⁺–SO₂–H₂O system, but in the presented

model the influence of carbonate/bicarbonate species on the sulfite species equilibrium was neglected; the concentration of the SO_4^{2-} was taken to be constant (due to the supersaturation of $CaSO_4$ and its crystallization) and its effect on the equilibrium was also neglected. The solubility curve for the $CaSO_3 \cdot 1/2\ H_2O$ was also presented in the equilibrium diagram.
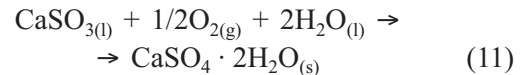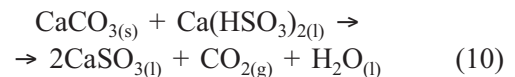
In the diagram for the Ca²⁺–SO₂–H₂O system the molar concentrations instead of the weight concentrations were used, the range of the diagram for this system had to be smaller due to the more dilute solutions present in the limestone scrubbing process.

For this system the process of absorption was divided into three partial processes as follows;

The overall reaction

$$SO_{2(g)} + CaCO_{3(s)} + 1/2O_{2(g)} + 2H_2O_{(l)} \rightarrow$$
$$\rightarrow CaSO_4 \cdot 2H_2O_{(s)} + CO_{2(g)} \qquad (8)$$

was divided into three partial reactions[9];

$$SO_{2(g)} + H_2O_{(l)} + CaSO_{3(l)} \rightarrow Ca(HSO_3)_{2(l)} \quad (9)$$

$$CaCO_{3(s)} + Ca(HSO_3)_{2(l)} \rightarrow$$
$$\rightarrow 2CaSO_{3(l)} + CO_{2(g)} + H_2O_{(l)} \qquad (10)$$

$$CaSO_{3(l)} + 1/2O_{2(g)} + 2H_2O_{(l)} \rightarrow$$
$$\rightarrow CaSO_4 \cdot 2H_2O_{(s)} \qquad (11)$$

Reaction (9) represents the absorption of SO_2 and the sulfite to bisulfite reaction, it takes place at constant c_{com}, the explanation is similar as for the reaction (5) in the MgO–SO₂–H₂O system. The reaction (10) represents the limestone dissolution and its reaction with $Ca(HSO_3)_2$, it occurs at constant c_{tot}. The third partial process – absorption of O_2, oxidation of $CaSO_3$ from the absorption process and the gypsum crystallization – is represented by the reaction (11) and occurs at constant *Y*.

It was assumed that these three partial processes take place in series and independently from each other. The crystallization of gypsum was not regarded as a separate partial process, it was assumed to take place simultaneously with the sulfite oxidation. These three partial processes can be presented as a triangle in the equilibrium diagram.

The industrial spray scrubbing process is presented in Fig. 3. The flue gas from the power plant flows through six spray levels and leaves the absorption unit. The limestone slurry flows countercurrent to flue gas and is collected in a holding tank, where air is also blown into to ensure the oxidation of sulfite into sulfate. Limestone slurry is pumped to the hydrocyclones, where the gypsum is
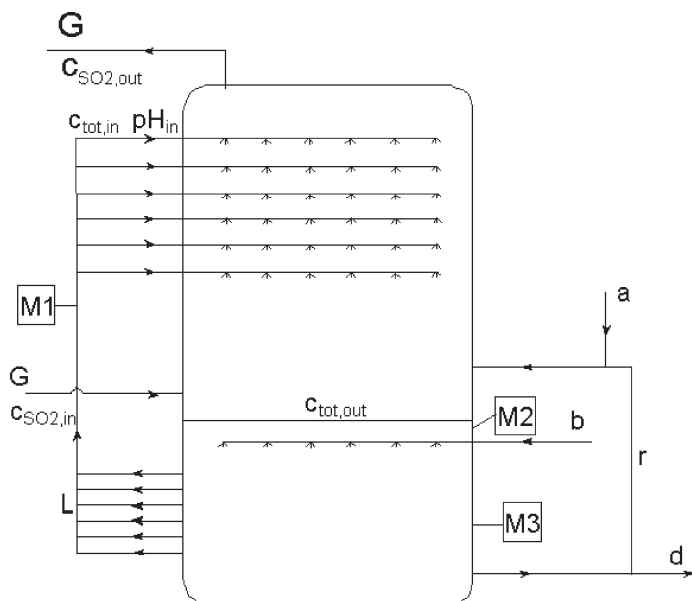
F i g . 3 – *Schematic flow diagram of industrial plant*
a – limestone, b – air, d – product (gypsum),
r – recycle

T a b l e 1 – *The basic process and triangle points data*

Process data	
$Q_G = 1.1 \cdot 10^6$ m³ h⁻¹	$c_{SO_2,in} = 0.125$ mmol l⁻¹
$Q_L = 5 \cdot 10^4$ m³ h⁻¹	$c_{SO_2,out} = 0.0041$ mmol l⁻¹

Triangle points		
	measured	calculated
M1	$c_{tot,in} = 6.24$ mmol l⁻¹, pH$_{in}$ = 6.0	$c_{com} = 3.59$ mmol l⁻¹
M2	/	$c_{tot,out} = 8.90$ mmol l⁻¹, pH$_{out}$ = 2.65*, $c_{com} = 3.59$ mmol l⁻¹
M3	/	$c_{tot,3} = 8.90$ mmol l⁻¹, pH$_3$ = 5.7*, $c_{com,3} = 4.90$ mmol l⁻¹

* from the equilibrium diagram

separated from the system, and then pumped again to the sprayers. Fresh limestone slurry is also added into the holding tank.

The experimental samples, taken from the industrial plant, were used as a basic point (M1) for the presentation of the mass balances. The other two triangle points (M2, M3) were obtained by the calculation procedure and can also be read from the equilibrium diagram. In such a way the mass balances of the three partial processes were presented in the equilibrium diagram (Fig. 4). The triangle represents an idealized operation of the industrial absorption plant. The data needed for the presentation are given in Table 1.
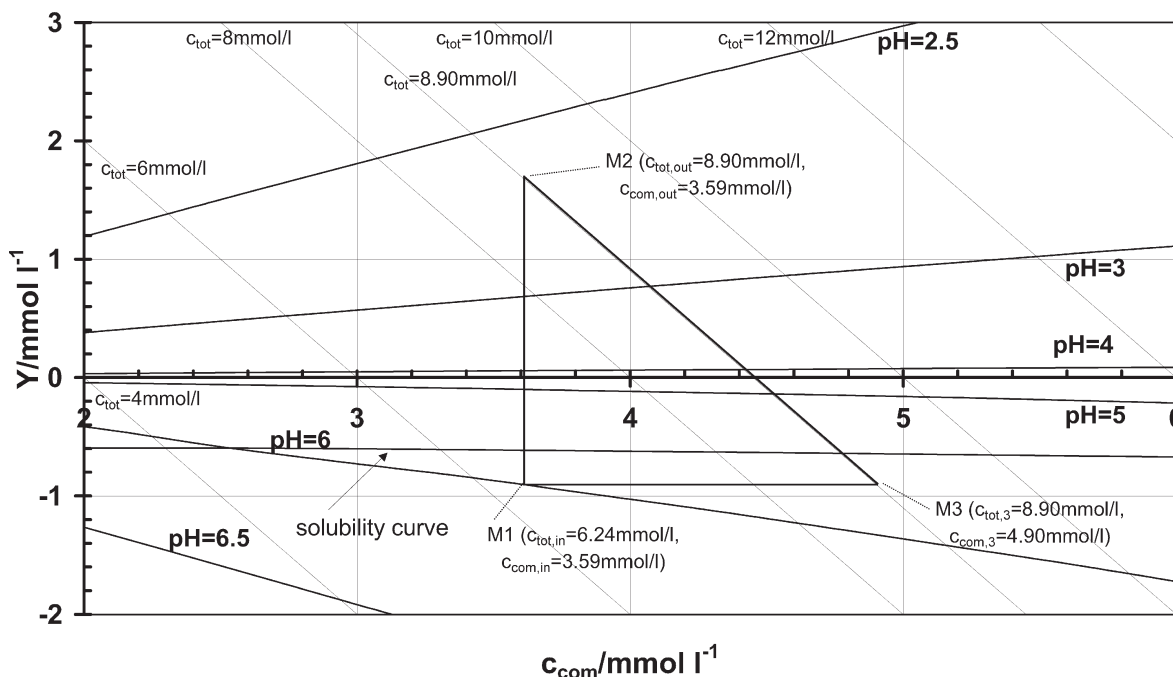

F i g . 4 – *Idealized presentation of the partial processes in the spray scrubbing process in the equilibrium diagram for the Ca²⁺–SO₂–H₂O system at 25°C⁹*
M₁M₂ – absorption of SO₂, sulfite – bisulfite reaction
M₂M₃ – limestone dissolution, reaction with Ca(HSO₃)₂
M₃M₁ – absorption of O₂, oxidation of CaSO₃, gypsum crystallization

T a b l e 2 – *The results of the mass transfer analysis for the three partial processes*

	K_{ov}	A	c_{pot}	F
absorption of SO₂	$K_g = 2.8 \cdot 10^{-2}$ m s^{-1}	$A_{SO_2} = 6.46 \cdot 10^4$ m^2	$c_{pot\,SO_2(ln)} = 0.0228$ mol m^{-3}	$F_{SO_2} = 150$ kmol h^{-1}
dissolution of CaCO₃	$k_s = 2.94 \cdot 10^{-3}$ m s^{-1}	$A_{CaCO_3} = 6.28 \cdot 10^6$ m^2	$c_{pot\,dissol} = 2.0 \cdot 10^{-3}$ mol m^{-3}	$F_{CaCO_3} = 133$ kmol h^{-1}
absorption of O₂	$k_{L(O_2)} = 3.8 \cdot 10^{-4}$ m s^{-1}	$A_{O_2} = 1.6 \cdot 10^5$ m^2	$c_{pot\,O_2(ln)} = 0.26$ mol m^{-3}	$F_{O_2} = 57$ kmol h^{-1}

The mass transfer analysis for all three partial processes was also made. It was assumed that mass transfer is the rate determining process (mass transfer is diffusion controlled), so the partial processes were modeled by a form of the equation[9]

$$F = K_{ov} \cdot A \cdot c_{pot} \qquad (12)$$

The data for the calculation were taken from the industrial absorption plant (Table 1), some data and the appropriate correlations were taken from the up to date literature.

The results of the calculation of the overall mass transfer coefficient K_{ov}, the area available for the mass transfer A, the concentration potential c_{pot} and the molar flow F for the three partial processes are presented in Table 2[9].

The results of the mass transfer analysis were verified with the basic mass balance equation;

$$Q_G(c_{SO_2,in} - c_{SO_2,out}) = Q_L(c_{tot,out} - c_{tot,in}) \qquad (13)$$

This equation gave a flow of sulfur dioxide 8500 kg SO₂/h or 133 kmol SO₂/h. According to the overall reaction (8) the flow of oxygen was 66.5 kmol O₂/h or 2100 kg O₂/h and the flow rate of CaCO₃ was 133 kmol CaCO₃/h or 13300 kg CaCO₃/h.

The results of the mass transfer analysis differ less than 15% from the values obtained with the calculation with equations (8) and (13) thus the presented model described the process satisfactory.

Comparison of the two systems

The thermodynamic model was developed for the MgO–SO₂–H₂O system and it described the equilibrium satisfactory. It enabled the construction of the equilibrium diagram which was suitable for the presentation of the mass balances of the partial processes. In the model the variables c_{tot}, c_{com}, and Y were proven to be convenient for description and presentation of the mass balances. The model was useful for constructing the diagrams for the Ca²⁺–SO₂–H₂O system without major changes. For this system the molar concentrations instead of weight concentrations were used and the concentration range for the diagrams is much smaller since it is defined by the low solubility of limestone. The diagrams were proven to be of great use for both systems, although the both industrial processes have important differences – the magnesium based process is regenerative and uses Venturi absorbers, the calcium based process is not regenerative and takes place in a spray scrubber. The diagrams give a basis for the quantitative idealized presentation of the processes and further analysis and thus offer a better understanding of the processes.

Nomenclature

c – concentration, wt%, mmol l^{-1}
A – area, m^2
c_{pot} – concentration potential, mol m^{-3}
Q_G – gas flow rate, m^3 h^{-1}
K_{ov} – overall mass transfer coefficient, m s^{-1}
K_g – overall mass transfer coefficient for SO₂ absorption, m s^{-1}
$k_{L(O_2)}$ – liquid–side mass transfer coefficient for O₂ absorption, m s^{-1}
k_S – liquid–side mass transfer coefficient for CaCO₃ dissolution, m s^{-1}
Q_L – liquid flow rate, m^3 h^{-1}
   – molar flow rate, kmol h^{-1}
Y – concentration of true free SO₂, wt%, mmol l^{-1}

Subscripts

   – comcombined SO₂
   – tottotal SO₂

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