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Model of oxygen absorption into calcium sulfite solutions [1]

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Abstract

Wet limestone scrubbing is the most common flue gas desulfurization process, and in this process sulfite oxidation plays a major role determining the dewatering properties of the sludge produced and leading to the production of gypsum of high quality. A literature analysis showed that the results obtained for sulfite oxidation under homogeneous conditions are relatively easily interpreted, while the results relative to heterogeneous reaction conditions (i.e. conditions in which gaseous oxygen and a sulfurous solution are brought in contact) are much more difficult to interpret, owing to the interaction between mass transfer and chemical reaction. In this work a model is proposed to describe the interaction between oxygen absorption and the oxidation reaction under heterogeneous conditions, which takes into account the peculiar characteristics of absorption with zero order reaction. A kinetic equation of order zero in dissolved O_2, 3/2 in HSO_3^- and 3/2 in the catalyst concentration was used to match experimental results presented in the literature and model results. Integration of the model equations led to evaluation of the oxygen absorption rate as a function of the catalyst concentration together with the concentration profiles in the liquid film for the different species. © 1997 Elsevier Science S.A.

Keywords: Oxygen absorption; Calcium sulphite

1. Introduction

Treatment of flue gas from power plants is required in order to reduce sulfur dioxide emissions into the atmosphere. Presently, the most common commercial process for the removal of SO_2 from stack gas is the wet limestone flue gas desulfurization process, in which oxidation of sulfite represents an important rate phenomenon. Detailed knowledge of the oxidation process is important for determination of the dewatering properties of the sludge produced, and a good understanding of the oxidation kinetics is also useful for the development of computer codes aimed at modeling the whole flue gas desulfurization process. The following overall reactions represent bisulfite and sulfite ion oxidation in aqueous solutions:

$$HSO_3^- + \tfrac{1}{2}O_2 = HSO_4^- \qquad (1)$$

$$SO_3^{2-} + \tfrac{1}{2}O_2 = SO_4^{2-} \qquad (2)$$

The kinetics of such reactions, and particularly of the absorption of oxygen by basic solutions of sodium sulfite in the presence of catalysts, has received great attention during the last 30 years. Linek and Vacek [1] presented a detailed review of the literature for the period 1960–1980. The interest in sodium sulfite oxidation has been due to the possibility of using this reaction to measure the interfacial area in gas–liquid contact devices: since oxygen absorption takes place in the fast reaction regime, its rate is proportional to the interfacial area [2]. The researchers who studied sulfite oxidation pointed out the extreme sensitivity of its kinetics to experimental conditions, which often prevented the achievement of reproducible results. It has been shown that the liquid phase composition (sulfite concentration, dissolved oxygen, pH), temperature, and presence, even in trace amounts, of catalysts ($Co^{2+}, Cu^{2+}, Mn^{2+}$) and inhibitors (alcohols, phenols, hydroquinone) strongly affect the reaction rate.

The literature results relative to homogeneous conditions (realized contacting a sulfite solution with an oxygen saturated solution) can be interpreted by means of the chain reaction mechanism proposed by Bäckstrom [3] and modified by Dogliotti and Hayon [4]. This mechanism assumes that oxidation takes place through complex radicalic reactions for which the initiation is represented by the auto-oxidation of catalytic species from M^{z+} to $M^{(z+1)+}$, or by the action of UV light [5]. This hypothesis is also strengthened by the

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extreme sensitivity of the reaction rate to free radical scavengers such as alcohols, phenols and hydroquinone [6–9]. The mechanism of Dogliotti and Hayon [4] takes into account the following reactions:

Formation of $M^{(z+1)+}$

$$2M^{z+} + O_2 + 2H^+ = 2M^{(z+1)+} + H_2O_2 \tag{3}$$

Initiation

$$M^{(z+1)+} + HSO_3^- = M^{z+} + HSO_3 \tag{4}$$

Propagation

$$HSO_3 + O_2 = HSO_5 \tag{5}$$

$$HSO_5 + HSO_3^- = HSO_4^- + HSO_4 \tag{6}$$

$$HSO_4 + HSO_3^- = HSO_3 + HSO_4^- \tag{7}$$

Termination

$$2HSO_3^- = \text{inactive products} \tag{8}$$

$$2HSO_4^- = \text{inactive products} \tag{9}$$

$$2HSO_5 = \text{inactive products} \tag{10}$$

The global reaction rate can be limited by one or another step, depending on the conditions under which the reaction takes place.

Moreover, depending on whether the oxidation reaction is operating at high pH or low pH, the dominant species undergoing oxidation is either the sulfite or the bisulfite ion respectively; since the typical conditions of flue desulfurization processes are at pH < 5, the prevailing species is the bisulfite ion, and in such circumstance the kinetics of the oxidation reaction was found to be proportional to the bisulfite concentration [10–12].

The researchers presented different overall rate equations, and there is no general agreement on what the oxidation kinetics are, even though most of them agree on the fact that the oxidation reaction is zero order in oxygen. Barron and O'Hern [13] proposed the following rate equation:

$$r = kc_M^{1/2} c_{HSO_3^-}^{3/2} \tag{11}$$

where r is the reaction rate, k is the kinetic constant, c_M the concentration of catalysts such as Co^{2+} and Mn^{2+}, and c_{HSO_3-} is the bisulfite ion concentration. Eq. (11) is obtained from the mechanism of Dogliotti and Hayon with the following assumptions: (i) the concentrations of the unstable intermediates are stationary; (ii) reaction 3 is at equilibrium; (iii) the limiting step is reaction 6; (iv) termination is caused by Eq. (10). Another kinetic equation is that found by Braga and Connick [8], of order 3/2 with respect to the manganese concentration. The authors suggested that the order 3/2 implies that manganese is involved in both the initiation and propagation steps. Pasiuk-Bronikowska and Ziajka [14] found that oxidation of aqueous sulfur dioxide catalyzed by manganous sulfate exhibits an order, with respect to the catalyst (Mn^{2+}), which varies from two to zero, depending on the manganese concentration. They ascribed the considerable confusion in the kinetic data for the oxidation process to the interaction between mass transfer and chemical reaction.

In order to describe sulfite oxidation under heterogeneous conditions, it is useful to study the interactions between absorption and chemical reaction in terms of the enhancement factor E, defined as the ratio of the observed liquid side mass transfer rate to the value which such a rate would have under the same driving force if no reaction took place [2]. Three regimes can be identified for absorption with chemical reaction, depending on the Hatta number Ha, which is defined as the ratio between the time available to diffusion and the time required by the reaction to change sensibly the liquid composition, or as the 'maximum possible conversion in the film compared with maximum transport through film' [15]. For $\text{Ha} \ll 1$ the absorption takes place in the slow reaction regime, and E is nearly equal to unity; for $\text{Ha} \gg 1$ the transition to the fast reaction regime occurs and $E > 1$; a further increase in Ha allows the transition to the instantaneous reaction regime and E reaches the upper bound E_∞ when all resistance to chemical reaction vanishes.

The aim of this work is to study the interaction between mass transfer and chemical reaction, proposing a numerical model which in particular takes into account the peculiar characteristics descending from the fact that the oxidation kinetics are zero order in oxygen. The model is capable of discerning among the three regimes described above, allowing a better understanding of the interaction between absorption and chemical reaction in sulfite oxidation.

2. Numerical model

The interaction between oxygen absorption and sulfite oxidation is modeled assuming that a clear calcium sulfite solution containing manganese sulfate as catalyst is brought in contact with a gaseous mixture of oxygen and an inert gas (e.g. nitrogen). The species which are present in the liquid phase are H^+, OH^-, $SO_{2(aq)}$, HSO_3^-, SO_3^{2-}, HSO_4^-, SO_4^{2-}, Ca^{2+}, Mn^{2+} and $O_{2(aq)}$, and among them the following ionic equilibria take place:

$$H_2O = H^+ + OH^- \tag{12}$$

$$SO_{2(aq)} + H_2O = H^+ + HSO_3^- \tag{13}$$

$$HSO_3^- = H^+ + SO_3^{2-} \tag{14}$$

$$HSO_4^- = H^+ + SO_4^{2-} \tag{15}$$

Since ionic species are present, it is necessary to impose the condition of electroneutrality by writing

$$\sum_I z_I c_I = 0 \tag{16}$$

where z_I and c_I are the electric charge and the concentration of species I respectively.

If the film theory is used to model the liquid side mass transfer phenomena, the transport equations have to describe the simultaneous absorption and chemical reactions which

Table 1
Diffusivity coefficients in water at 298 K and the normalized values $Đ$

Species	$D\times10^9$ ($m^2\,s^{-1}$)	$Đ\times10^9$ ($m^2\,s^{-1}$)
H^+	9.30 [17]	4.92
OH^-	5.27 [17]	3.70
$SO_{2(aq)}$	1.76 [18]	2.14
HSO_3^-	1.33 [17]	1.86
SO_3^{2-}	0.77 [17]	1.41
HSO_4^-	1.33 [19]	1.86
SO_4^{2-}	1.06 [19]	1.66
O_2	2.6 [20]	2.6
Ca^{2+}	0.79 [17]	1.43

take place in a stagnant film of thickness δ adhering to the gas–liquid interface. Such equations can be written in the form

$$\frac{dN_I}{dx}=-r_I \tag{17}$$

where N_I is the molar flux of the species I, x is the normal coordinate in a system having its origin at the gas–liquid interface, and r_I is the rate at which the I species is produced by chemical reactions. Since ten species are present in the reactor, a system of ten equations in ten unknown concentrations is to be solved.

It is worth noting that in transport processes involving charged species, the molar flux of the I species should be expressed not by Fick's law, but by means of the following expression [16]:

$$N_I=-D_I\frac{dc_I}{dx}-F\frac{D_I}{RT}z_Ic_I\frac{d\Phi}{dx} \tag{18}$$

where D_I is the diffusivity of I species reported in Table 1, F is the Faraday constant, and R is the gas constant.

It is worth noting that all diffusivities D were normalized $Đ$ with respect to the diffusivity of oxygen by using the following expression:

$$Đ_I=D_{O_2}\sqrt{D_I/D_{O_2}} \tag{19}$$

In this way it was possible to approximate accurately, using the film theory, the solutions obtained with the penetration theory, as shown by Chan and Rochelle [21].

Since the condition that there is no net charge transport from and to the gas–liquid interface is expressed as

$$\sum_I z_IN_I=0 \tag{20}$$

it results that the following expression for the gradient of electric potential $d\Phi/dx$, proposed by Vinograd and MacBain [22], should be used:

$$\frac{d\Phi}{dx}=-\frac{\sum_I z_ID_I\,dc_I/dx}{F\sum_I z_I^2(D_I/RT)c_I} \tag{21}$$

from which it is obtained that the gradient of electric potential is not zero since the diffusivities are not equal among them. However, as showed by Rochelle and coworkers [23,24], if Fick's law is used to express the molar flux, and the electroneutrality equation (Eq. (16)) is substituted by the following equation stating the absence of net charge transport

$$\frac{d}{dx}\left(\sum_I z_IN_I\right)=0 \tag{22}$$

the results are only slightly affected, but it is possible to decouple the transport Eq. (17) and therefore to solve it more easily. For this reason, integration of the equations of the model was carried out following this approach.

Since reactions 12–15 are proton exchange reactions and as such very fast, it is possible to consider them as instantaneous reactions and then to apply the 'total material balance' approach introduced by Olander [25]. In this way, instead of writing three differential equations for the sulfurous species $SO_{2(aq)}$, HSO_3^- and SO_3^{2-}, it is possible to use just a single differential equation associated with the two algebraic equations relative to the equilibria of reaction 13 and reaction 14. Similarly, for the species HSO_4^- and SO_4^{2-}, it is possible to use just one transport equation, associated with the equilibrium equation relative to Eq. (15). Eventually, concerning H^+ and OH^-, the two transport equations can be replaced by the algebraic equation relative to the equilibrium of Eq. (12) and by the equation stating that there is no charge generation in the film.

The model is therefore described by the following set of equations:

$$\frac{dN_{O_2}}{dx}=-r_{ox} \tag{23}$$

$$\frac{d}{dx}(N_{SO_{2(aq)}}+N_{HSO_3^-}+N_{SO_3^{2-}})=-2r_{ox} \tag{24}$$

$$\frac{d}{dx}(N_{HSO_4^-}+N_{SO_4^{2-}})=2r_{ox} \tag{25}$$

$$\frac{d}{dx}(N_{Ca^{2+}})=0 \tag{26}$$

$$\frac{d}{dx}(N_{Mn^{2+}})=0 \tag{27}$$

$$\frac{d}{dx}\left(\sum_I z_IN_I\right)=0 \tag{28}$$

where, in order to avoid a finite reaction rate when no oxygen is present, the reactive term r_{ox} is expressed as the product between the reaction rate and the step function, following the approach of Astarita and Marrucci [26].

Manipulating Eqs. (23)–(28), the system to be solved becomes:

$$\frac{dN_{O_2}}{dx} = -r_{ox} \tag{29}$$

$$\frac{dN_{S(IV)}}{dx} + \frac{dN_{S(VI)}}{dx} = 0 \tag{30}$$

$$\frac{dN_{S(IV)}}{dx} - 2\frac{dN_{O_2}}{dx} = 0 \tag{31}$$

$$\frac{dN_{Ca^{2+}}}{dx} = 0 \tag{32}$$

$$\frac{dN_{Mn^{2+}}}{dx} = 0 \tag{33}$$

$$\frac{d\left(\sum_l z_l N_l\right)}{dx} = 0 \tag{34}$$

where $N_{S(IV)}$ and $N_{S(VI)}$ refer to the total sulfite and total sulfate respectively. Eq. (29) considers oxygen consumption due to oxidation; Eq. (30) expresses the absence of sulfur generation in the liquid film; Eq. (31) depends on the stoichiometry of the oxidation reaction; Eqs. (32) and (33) express the absence of Ca^{2+} and Mn^{2+} transport; Eq. (34) expresses the condition that no net charge transport takes place between the liquid and the gas.

The boundary conditions for the system of Eqs. (29)–(34) are the following: (i) at $x=0$

$$c_{O_2} = p_{O_2}/H_{O_2} \tag{35}$$

$$N_{S(IV)} + N_{S(VI)} = 0 \tag{36}$$

$$N_{S(IV)} = 0 \tag{37}$$

$$N_{Ca^{2+}} = 0 \tag{38}$$

$$N_{Mn^{2+}} = 0 \tag{39}$$

$$\sum_l z_l N_l = 0 \tag{40}$$

(ii) at $x = \delta$, where δ is the film thickness

$$c_{O_2} = c_{O_2}|_{bulk} \tag{41}$$

$$c_{S(IV)} + c_{S(VI)} = c_{S(IV)}|_{bulk} + c_{S(VI)}|_{bulk} \tag{42}$$

$$c_{S(IV)} = c_{S(IV)}|_{bulk} \tag{43}$$

$$c_{Ca^{2+}} = c_{Ca^{2+}}|_{bulk} \tag{44}$$

$$c_{Mn^{2+}} = c_{Mn^{2+}}|_{bulk} \tag{45}$$

$$\sum_l z_l c_l = 0 \tag{46}$$

Eq. (35), in which p_{O_2} and H_{O_2} are the oxygen partial pressure and Henry's constant respectively, states that for oxygen transport the gas side mass transfer resistance is neglected, and Henry's law is used to express the composition at the interface; Eqs. (36)–(40) state that there is no transport through the gas–liquid interface of sulfite, sulfate, calcium, manganese and electric charges; Eqs. (41)–(46) relate the film and bulk concentration at their boundary.

The oxygen bulk concentration was determined from an equation for the oxygen flux through the film–bulk boundary, derived from Froment and Bishoff [27]:

$$aVN_{O_2}|_{x=\delta} = V(1-a\delta)r_{ox} + Lc_{O_2}|_{x=\delta} \tag{47}$$

This balance refers to a mixed tank reactor of liquid hold-up V, with a specific contact area a and a liquid flow rate L. The last term of the equation is the net amount of O_2 which flows with the liquid.

3. Results

The integration of the system of Eqs. (29)–(34) can be carried out using a finite difference numerical technique; the integration leads to evaluation of the oxygen absorption rate as a function of the catalyst concentration and furthermore allows calculation of the concentration profiles in the liquid film of the different species. In order to validate the model proposed, its results were compared with the experimental results presented by Pasiuk-Bronikowska and Ziajka [28]; these authors studied sulfite oxidation in a stirred-tank absorber with a plane gas–liquid interface; the gas phase was a mixture of O_2 and N_2 at atmospheric pressure, while the liquid phase was a clear solution of $CaSO_3$ with $MnSO_4$ added as catalyst; the liquid hold-up was 1.0×10^{-3} m^3, the specific contact area was $a = 7.1$ m^{-1}, k_L^0 was 1.5×10^{-5} m s^{-1}, the film thickness was $\delta = 1.73 \times 10^{-4}$ m and therefore the Hinterland ratio, defined as the ratio between the total phase volume and the reaction phase film volume ($Al = (1-\epsilon)/a\delta$, where $1-\epsilon$ is the fraction reaction rate) [29], was $Al = 812$. The value of the instantaneous enhancement factor was $E_\infty = 24.5$.

In Fig. 1 the oxygen absorption rate is reported as a function of Mn^{2+} concentration, showing the comparison between the experimental results of Pasiuk-Bronikowska and Ziajka [28] and the model results. In this figure it is possible to identify the kinetic and the diffusional subregimes, the fast reaction regime, and the transition to the instantaneous reaction regime. The following rate equation was used in the model:

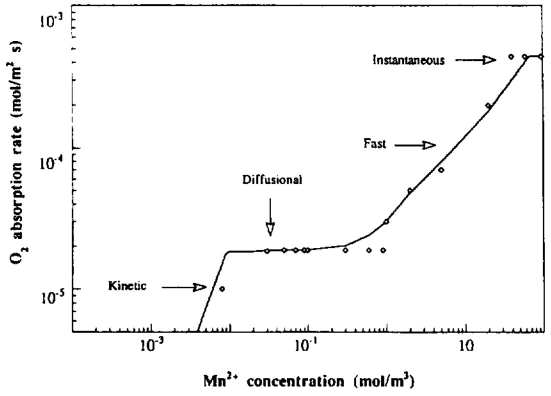

Fig. 1. O_2 absorption rate vs. Mn^{2+} concentration: ◇ experimental results; — model results; $c_{S(IV)} = 82$ mol m^{-3}, $c_{Ca^{2+}} = 120$ mol m^{-3}, $p_{O_2} = 0.96$ atm and pH 3.8

$$r_{\mathrm{ox}}=kc_{\mathrm{Mn}^{2+}}^{3/2}c_{\mathrm{HSO}_3^-}^{3/2} \tag{48}$$

where the value of the kinetic constant k ($k=3.0\times10^{-5}$ $\mathrm{m^3\,mol^{-1}\,s^{-1}}$) and the order of reaction with respect to Mn^{2+} were evaluated by fitting the theoretical curve to the experimental results. It is worth noting that the model contains just one parameter k, yet it is able to describe the three regimes mentioned above and the transitions between them. Model and experimental results show that in the slow kinetic reaction regime a dependence of order 1.5 exists between the oxygen absorption rate and the catalyst concentration, while in the fast reaction regime this dependence becomes of order 0.75, in agreement with the theory of mass transfer with chemical reaction [30].

In Fig. 2 the oxygen concentration profiles in gas–liquid film are reported for different values of the Hatta number, defined by the following equation:

$$\mathrm{Ha}=\sqrt{\frac{D_{\mathrm{O}_2}k(c_{\mathrm{Mn}^{2+}}|_{\mathrm{b}}\,c_{\mathrm{HSO}_3^-}|_{\mathrm{b}})^{3/2}}{(k_{\mathrm{L}}^{\mathrm{o}})^2c_{\mathrm{O}_2}|_{\mathrm{i}}}} \tag{49}$$

where D_{O_2} is the oxygen diffusivity and the subscripts b and i refer to bulk and gas liquid interface respectively.

Three kinds of O_2 concentration profile can be distinguished, as pointed out by Landau [31]: for low values of $c_{\mathrm{Mn}^{2+}}$, and therefore Ha, the reaction does not go to completion in the film, and therefore the O_2 concentration in the liquid bulk is not zero; for intermediate values of Ha, c_{O_2} becomes zero at the film–bulk interface, but its gradient is not zero, and an instantaneous oxygen consumption takes place at such interface; eventually, for high values of Ha, the oxygen concentration becomes zero in the liquid film.

In Fig. 3(a) and (b) the concentration profiles of all the species involved in the process are reported in a dimensional and dimensionless way. In particular, in Fig. 3(b) the concentrations of all species were made dimensionless with respect to their bulk values, except for the oxygen concentration, which was made dimensionless with respect to its value at the gas–liquid interface. The figures refer to a condition of $c_{\mathrm{Mn}^{2+}}=5\ \mathrm{mol\ m^{-3}}$ and therefore $\mathrm{Ha}=1.438$. They show that two zones can be distinguished in the film. In the first zone, characterized by the presence of dissolved oxygen ($0<x/\delta<0.4$), the oxidation reaction takes place, and sulfate is produced at the expense of the bisulfite ion HSO_3^-. In the second zone ($0.4<x/\delta<1$) no oxidation takes place, and the concentration profiles essentially respect the condition that sulfite is to be transported from the liquid bulk to the gas–liquid interface, while sulfate is to be transported in the opposite direction. However, in this zone too the concentration profiles are curved, owing to the fact that oxidation consumes a weak acid (HSO_3^-), to produce a much stronger acid (HSO_4^-). This causes a decrease in the solution pH, which in turn determines a variation of the concentrations with respect to the ionic equilibria (Eqs. (12)–(15)).

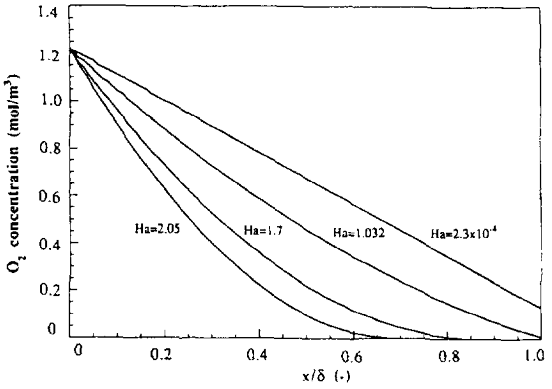

Fig. 2. Oxygen concentration in the liquid film; $c_{\mathrm{S(IV)}}=82\ \mathrm{mol\ m^{-3}}$, $c_{\mathrm{Ca}^{2+}}=120\ \mathrm{mol\ m^{-3}}$, $p_{\mathrm{O}_2}=0.96$ atm and pH 3.8.

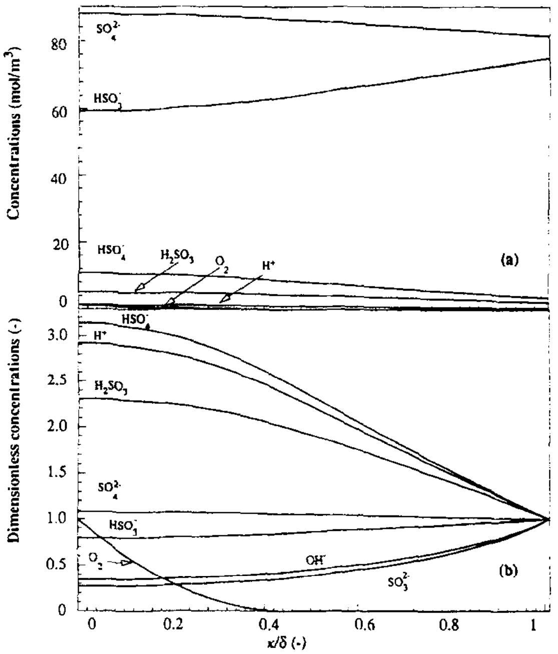

Fig. 3. Concentration profiles of the different species in the liquid film: (a) dimensional concentrations; (b) dimensionless concentrations. $c_{\mathrm{Ca}^{2+}}=120\ \mathrm{mol\ m^{-3}}$, $c_{\mathrm{Mn}^{2+}}=5\ \mathrm{mol\ m^{-3}}$ and $p_{\mathrm{O}_2}=0.96$ atm.

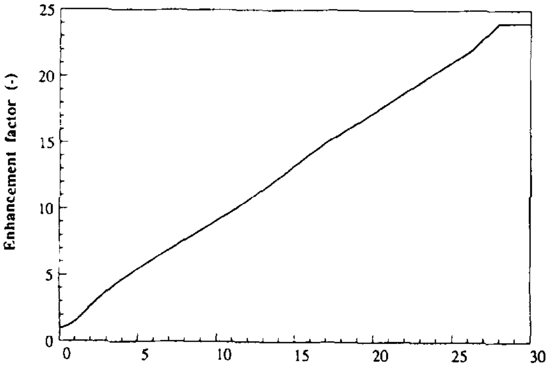

Fig. 4. Enhancement factor vs. Hatta number; $c_{\mathrm{S(IV)}}=82\ \mathrm{mol\ m^{-3}}$, $c_{\mathrm{Ca}^{2+}}=120\ \mathrm{mol\ m^{-3}}$, $p_{\mathrm{O}_2}=0.96$ atm and pH 4.0.

In Fig. 4 the model results are used to determine the dependence of the enhancement factor E on the Hatta number. The curve shows that for low values of Ha the absorption occurs in the slow reaction regime, and therefore E is nearly equal to unity, while for higher values of Ha the fast reaction regime takes place, with E equal to Ha; in the rightmost section of the figure the dependence of E on Ha is attenuated, indicating that, for very high reaction rates, HSO_3^- transport becomes limiting, and the transition to the instantaneous reaction regime takes place.

The model results have also been compared with the approximate solution presented by Hikita and Asai for the evaluation of the gas absorption rate and of the enhancement factor. The comparison between the model of Hikita and Asai [32] and the model proposed in our paper showed that, while in the slow reaction regime the two models give similar results, in the fast reaction regime a difference of about 25% exists in the calculation of the enhancement factor. It is to be recognized that the model of Hikita and Asai gives an approximate solution of the equations which describe the theory of mass transfer with chemical reactions, while the model presented in the paper gives a rigorous solution and allows calculation of the concentrations profiles of all the species involved in the process.

4. Conclusions

The study of sulfite oxidation under conditions typical of flue gas desulfurization processes is particularly relevant because it influences the overall rate in an FGD plant. A literature analysis showed that it is relatively easy to interpret the results obtained under homogeneous conditions by means of the kinetic Eq. (11). However, results relative to heterogeneous reaction conditions are much more difficult to interpret, owing to the interaction between mass transfer and chemical reaction. In this work a model was proposed to describe such interaction, which considers the peculiar characteristics of absorption with zero order reaction. A kinetic equation, of order 3/2 with respect to both catalyst concentration and sulfite concentration, was used, allowing the evaluation of the oxygen absorption rate as a function of the catalyst concentration. Moreover, the concentration profiles of all the species involved were evaluated.

5. Symbols

a	Specific contact area, m^{-1}
Al	Hinterland ratio, dimensionless
c	Concentration, mol m^{-3}
D	Diffusivity, $m^2\ s^{-1}$
$\bar{D}$	Normalized diffusivity (see Eq. (19)), $m^2\ s^{-1}$
E	Enhancement factor, dimensionless
E_∞	Instantaneous enhancement factor, dimensionless
F	Faraday constant, A s mol^{-1}
Ha	Hatta number, dimensionless
k	Kinetic constant, $m^3\ mol^{-1}\ s^{-1}$ (Eq. (11)) or $m^6\ mol^{-2}\ s^{-1}$ (Eq. (48))
k_L^o	Liquid side mass transfer coefficient, m s^{-1}
N	Molar flux, mol $m^{-2}\ s^{-1}$
p	Partial pressure, atm
r	Reaction rate, mol $m^{-3}\ s^{-1}$
R	Gas constant, m^3 Pa $mol^{-1}\ K^{-1}$
R_{O_2}	Oxygen absorption rate, mol $m^{-2}\ s^{-1}$
T	Temperature, K
x	Normal coordinate in the film, m
z	Electric charge, dimensionless

5.1. Greek symbols

δ	Film thickness, m
Φ	Electric potential, J $m^{-1}\ s^{-1}\ A^{-1}$

5.2. Subscripts

aq	Aqueous solution
b	Liquid bulk
M	Catalyst
S(IV)	Sulfite
S(VI)	Sulfate
I	I species
i	Gas–liquid interface
ox	Oxidation

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