

Limestone-Gypsum Flue Gas Desulfurization Process: Modeling of Catalyzed Bisulfite Oxidation

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The most common commercial process for SO₂ removal from flue gas is the wet limestone flue gas desulfurization process, in which sulfite oxidation represents an important limiting phenomenon. A detailed knowledge of the oxidation process is important to determine 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. Sulfite oxidation was studied both in homogeneous conditions, obtained by contacting a sulfite solution with an oxygen saturated solution, and in heterogeneous conditions, obtained by contacting a sulfurous solution with an oxygen containing gas phase. As far as the bisulfite oxidation reaction in heterogeneous conditions is concerned, a previous experimental study by the same research group in absolute catalyst free conditions found a kinetic equation for calcium bisulfite oxidation which is of zero order in oxygen and three halves in HSO₃⁻ ions. The reaction has then been carried out in the presence of other catalysts, namely manganese and ferrous ions, into a laboratory-scale well-mixed reactor. Experimental results have shown that, when catalyst concentration increases, three different reaction regimes (slow kinetic, slow diffusional and fast reaction regime) can be detected. This paper proposes a numerical model to describe the interaction between oxygen absorption and oxidation reaction, in which an in-parallel kinetic equation is used to describe the slow kinetic reaction results, according to which the overall reaction rate can be calculated as the sum of the uncatalyzed and catalyzed reaction rate, also taking into account that the oxidation kinetics are zero order in oxygen. Moreover, this paper shows how the model is capable of describing the experimental results obtained by this research group, as far as the manganese catalyzed bisulfite oxidation rate is concerned.

1. Introduction

The most common commercial process for SO₂ removal from flue gas is wet limestone flue gas desulfurization, in which sulfite oxidation represents an important limiting phenomenon. A detailed knowledge of the oxidation process is important to determine 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 (Yi et al., 2008; Fernández et al., 1997) (RIF). Sulphite oxidation rate significantly affects calcium sulphate super-saturation and hence the characteristics of the gypsum produced (Prisciandaro et al., 2001, 2009).

The kinetics of the absorption of oxygen by basic solutions of sodium sulfite in the presence of catalysts, received great attention during the last thirty years. 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. Sulfite oxidation was studied both in homogeneous conditions, obtained by contacting a sulfite solution with an oxygen-saturated solution, and in heterogeneous conditions, obtained by contacting a sulfurous solution with an oxygen-containing gas phase. The literature results relative to homogeneous conditions can be interpreted by means of a chain reaction mechanism. The researchers presented different overall rate equations, but there is no general agreement about the nature of oxidation kinetic reactions; however, in a previous work, this research group, in a literature review, showed that the following equation is the most appropriate to describe the kinetics of the homogeneous oxidation reaction for a pH range of 7.5 – 9 (Lancia and Musmarra, 1999):

$$r = kc_M^{1/2}c_{S(IV)}^{3/2} \quad (1)$$

where r is the reaction rate expressed as moles of SO_4^{2-} produced per unit of time and volume, k is the kinetic constant, c_M the catalyst concentration and $c_{S(IV)}$ the total sulfite concentration. Moreover there is only a partial agreement in the literature on the value of the kinetic constant at 25 °C, which ranges between 2×10^6 and 36×10^6 m^3/mol , while the activation energy ranges from 50 to 150 kJ/mol. As to the bisulfite oxidation reaction in heterogeneous conditions, a previous experimental study by the same research group in absolute catalyst free conditions has given the following kinetic equation for calcium bisulfite oxidation which is of zero order in oxygen and three halves in HSO_3^- ions (Lancia et al., 1997):

$$r_u = k_u c_{HSO_3^-}^{3/2} \quad (2)$$

where k_u is the uncatalyzed kinetic constant and $c_{HSO_3^-}$ the bisulfite ion concentration, with $k_u = 1.19 \times 10^{-4}$ $m^{3/2}/mol^{1/2} s$ at $T = 45$ °C. The reaction has then been carried out in the presence of other catalysts, namely manganese and ferrous ions, introduced both separately and together in solution, into a laboratory-scale well-mixed reactor. The results have been interpreted following the approach indicated by Astarita et al. (1983), i.e. when catalyst concentration increases, three different reaction regimes can be identified, the slow kinetic, the slow diffusional and the fast reaction regime, as well as the transition from one regime to another. In order to describe the three different regimes of reaction mentioned above, it is useful to make use of the enhancement factor E , defined as the ratio of the observed liquid side mass transfer rate to the value which such rate would have under the same driving force if no reaction took place. 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 markedly change the liquid composition or as the "maximum possible conversion in the film compared with maximum transport through film". For $Ha \ll 1$ the absorption takes place in the slow reaction regime, and E is nearly equal to 1; for $Ha \gg 1$ the transition to the fast reaction regime occurs and $E > 1$; a further increase of Ha allows the transition to the instantaneous reaction regime and E reaches the upper bound E_∞ when all resistance to chemical reaction vanishes.

This research group has already proposed a numerical model to describe the interaction between oxygen absorption and the oxidation reaction in heterogeneous conditions, in which a kinetic equation of order 0 in dissolved O_2 , $3/2$ in HSO_3^- and $3/2$ in the catalyst concentration was used (Lancia et al., 1997). This approach, which used an in series kinetic equation, was chosen to match experimental results presented in literature (Pasiuk-Bronikowska and Ziajka, 1989) and model results. The renewed model proposes a new approach, in which an in parallel kinetic equation is used to describe the slow kinetic reaction results, according to which the overall reaction rate can be calculated as the sum of the uncatalyzed and catalyzed reaction rate:

$$r = r_u + r_c = k_u c_{HSO_3^-}^{3/2} + k_c c_{Mn^{2+}} \quad (3)$$

where k_u is the kinetic constant of eq. (2), $c_{Mn^{2+}}$ the manganese ion concentration, k_c is the manganese catalyzed kinetic constant and with $k_c = 0.193 s^{-1}$ at $T = 45$ °C.

The aim of this work is to study the interaction between mass transfer and chemical reaction by proposing a renewed numerical model which considers a parallel mechanism between catalyzed and uncatalyzed reaction rate, also taking into account the peculiar characteristics descending from the fact that the oxidation kinetics are zero order in oxygen. Moreover, this paper shows how the model is capable of describing the experimental results obtained by this research group (Lancia et al., 2004; Karatza et al, 2008; Karatza et al., 2010) as to the manganese catalyzed bisulfite oxidation rate.

2. Model description

The detailed description of the equations used in the model and their resolution are reported in a previous paper (Lancia et al., 1997). In brief, 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:



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

$$\sum_I z_I c_I = 0 \quad (8)$$

where z_I and c_I are the electric charge and the concentration of the I species 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 take place in a stagnant film of thickness δ adhering to the gas-liquid interface. Such equations can be written in the form:

$$\frac{dN_I}{dx} = -r_I \quad (9)$$

where N_I is the molar flux of the I species, 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, with the relative boundary conditions. It is worth noting that in transport processes involving charged species, the molar flux of the I species cannot be expressed by using the Fick's law, but the gradient of electric potential is to be considered. However, as showed by Rochelle (1992) if the Fick's law is used to express the molar flux and the electro-neutrality equation (Eq. 8) is substituted by the following equation stating the absence of net charge transport:

$$\frac{d}{dx} (\sum_I z_I N_I) = 0 \quad (10)$$

the results are only slightly affected, but it is possible to decouple the transport equations (9) and therefore to solve it more easily. For this reason, the integration of the equations of the model was carried out following this approach. By using the total material balance approach, the model is therefore described by the following set of equations:

$$\frac{dN_{O_2}}{dx} = -r_{O_2} \quad (11)$$

$$\frac{dN_{S(IV)}}{dx} + \frac{dN_{S(VI)}}{dx} = 0 \quad (12)$$

$$\frac{dN_{S(IV)}}{dx} - 2 \frac{dN_{O_2}}{dx} = 0 \quad (13)$$

$$\frac{dN_{Ca^{2+}}}{dx} = 0 \quad (14)$$

$$\frac{dN_{Mn^{2+}}}{dx} = 0 \quad (15)$$

$$\frac{d}{dx} (\sum_I z_I N_I) = 0 \quad (16)$$

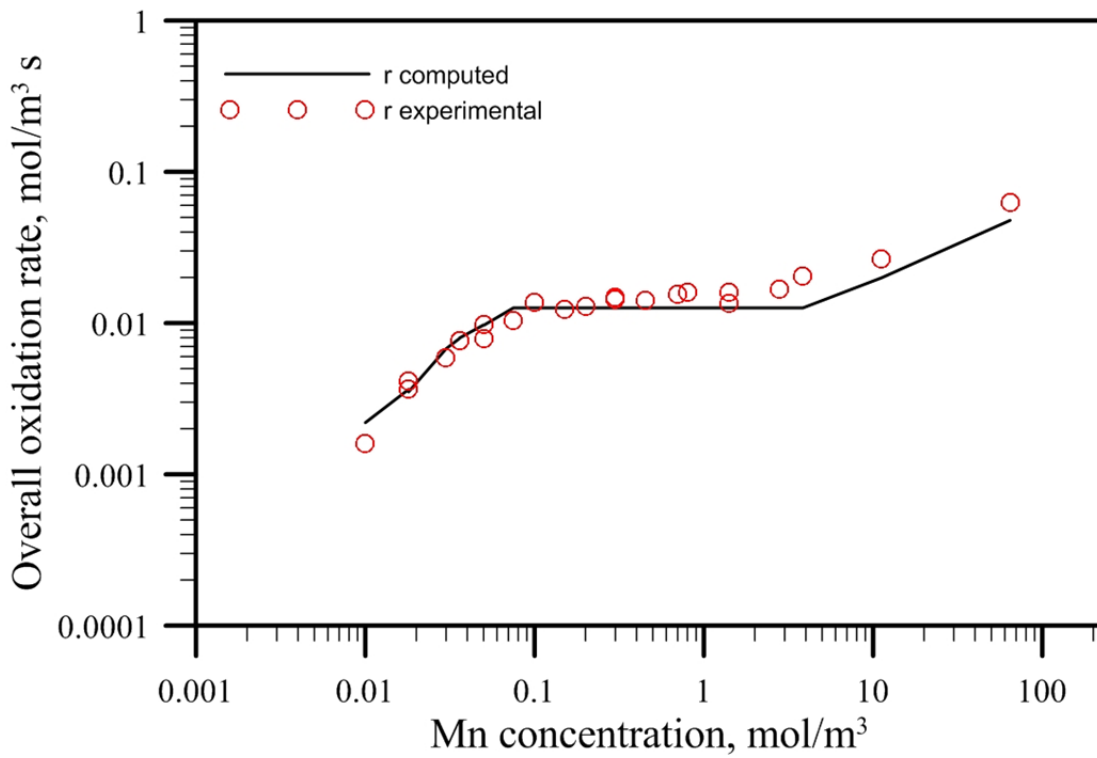


Figure 1: Overall reaction rate as a function of catalyst concentration; $p_{O_2}=21.3$ kPa.

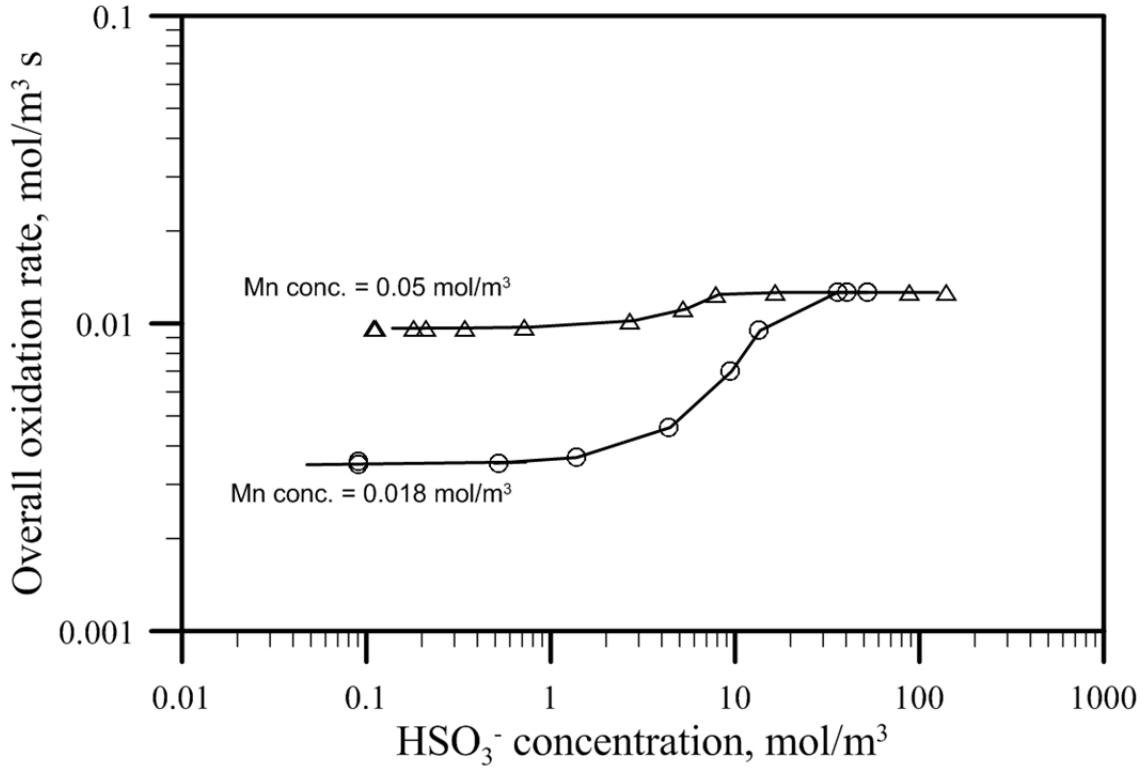


Figure 2: Overall reaction rate as a function of bisulfite concentration; $p_{O_2}=21.3$ kPa; \circ : $c_{Mn^{2+}}=0.018$ mol/m³; \triangle : $c_{Mn^{2+}}=0.05$ mol/m³.

3. Results

The integration of the system of equations is carried out by using a finite difference numerical technique; the integration leads to the evaluation of the oxygen absorption rate as a function of the catalyst concentration and furthermore allows to calculate 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 obtained by this research group (Lancia et al., 2004) as for the oxidation of calcium bisulfite in heterogeneous conditions, with MnSO_4 as a catalyst.

The simulated experimental conditions refer to the sulfite oxidation carried out in a stirred-tank absorber with a plane gas-liquid interface; the gas phase is a mixture of N_2 and O_2 with this last variable from 5 to 40%, while the liquid phase is a clear solution of CaSO_3 with MnSO_4 added as catalyst; the liquid holdup is $3.9 \times 10^{-4} \text{ m}^3$, the specific contact area is $a=510 \text{ m}^{-1}$, k_L^0 is $7.34 \times 10^5 \text{ m/s}$, the film thickness is $\delta=3.54 \times 10^{-5} \text{ m}$. In Figure 1 the oxygen absorption rate is reported as a function of Mn^{2+} concentration for oxygen partial pressure $p_{\text{O}_2}=21.3 \text{ kPa}$, showing the comparison between the experimental results of Lancia et al. (2004) and the model results. In this figure it is possible to identify the slow reaction regime (both kinetic and diffusional subregime) and the fast reaction regime. The rate equation (3) was used in the model; model and experimental results show that in the slow kinetic reaction regime a dependence of order 1 exists between the oxygen absorption rate and the catalyst concentration, while in the fast reaction regime such dependence becomes of order 0.5, in agreement with the theory of mass transfer with chemical reaction (Astarita et al., 1983).

In Figure 2 the comparison between experimental and model results is expressed in terms of reaction rate versus bisulfite ion concentration, for two different catalyst concentrations, i.e. $c_{\text{Mn}^{2+}}=0.05$ and 0.018 mol/m^3 . Figure 2 shows that model is again able to describe the marked catalytic effect exerted by Mn^{2+} , which is particularly evident at relatively low bisulfite concentration (below 7 mol/m^3), while it becomes less evident at higher values of $c_{\text{HSO}_3^-}$, where the difference between the catalyzed and the uncatalyzed reaction rate is almost negligible. For higher values of $c_{\text{HSO}_3^-}$ the reaction rate becomes practically coincident with the uncatalyzed rate reaching the ceiling of the diffusional subregime.

4. Conclusions

In this paper, a renewed version of the model describing oxidation in heterogeneous conditions – using manganese as a catalyst, is presented, a key step in wet limestone-gypsum desulfurization process. The model, which takes into account for the interactions between oxygen absorption and chemical reaction, considers a kinetic model that uses an *in parallel* approach, in which the oxidation rate is the sum of the uncatalyzed and the catalyzed reaction rate. Model results are compared with experimental results obtained by the same research group, which show the strong catalytic effect of manganese on the bisulfite oxidation rate.

5. Nomenclature

a	specific interfacial area, m^{-1}
a_l	activity of the l species, mol m^{-3}
c_l	concentration of the l species, mol m^{-3}
$c_{\text{O}_2^j}$	oxygen interfacial concentration, mol m^{-3}
c_M	catalyst concentration, mol m^{-3}
$c_{\text{S(IV)}}$	total sulfite concentration, mol m^{-3}
E	activation energy, kcal mol^{-1}
FI	ionic strength, mol m^{-3}
k	kinetic constant, according to reaction rate
k_L^0	liquid side mass transfer coefficient, m sec^{-1}
K	equilibrium constant
M^{2+}	catalytic species, (Co^{2+} , Fe^{2+} , Mn^{2+})
p	pressure, Pa
r	reaction rate, $\text{mol m}^{-3} \text{ sec}^{-1}$
R	overall oxidation rate, $\text{mol m}^{-3} \text{ sec}^{-1}$
T	temperature, $^{\circ}\text{C}$
z_l	electric charge, dimensionless

Greek letters

α_i stoichiometric coefficient of the i species, dimensionless

γ_i activity coefficient of the i species, dimensionless

τ liquid residence time, sec

Subscripts

u relative to uncatalyzed reaction

c relative to catalyzed reaction

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