

Improvements on the Modelling of Sulphur Dioxide Emissions from Fluidised Bed Combustors and Gasifiers

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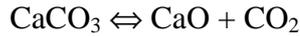
Abstract. *Sulphur dioxide emissions from Fluidised Bed Combustors (FBCs) can be drastically reduced by in-bed treatment with limestone or dolomite. The technique is now well established and extensive research has been conducted in this area. Models have been developed to express the rate of sulphur dioxide capture by limestone, however; such models typically require a fitting parameter in order to correlate the predicted to the experimental data. In the present work a sulphur capture model has been developed. The model has been implemented into the CSFB (Comprehensive Simulator for Fluidised-Bed) which is a code used in the simulation of industrial FBCs. The predicted and experimentally measured sulphur dioxide emission levels showed good agreement in all cases without the use of any fitting parameter. The model has also been used to investigate how the structure of limestone affects its ability to absorb sulphur dioxide within a FBC. It was found that structures, which represent geographically young limestones, absorb sulphur dioxide at higher rates and become deactivated at higher conversion levels than older limestone structures. Further work is being undertaken to see if this effect could explain the discrepancies experienced between different sulphur capture models.*

Keywords: Fluidised-Bed, Simulation, Sulphur capture, Modelling

1. INTRODUCTION

The Fluidised-Bed technique can be applied to a wide range of industrial processes. These include boilers, gasifiers, oil shale retorters and reactors using solid catalysts. Since the early 1960's, great interest has emerged for utilising the Fluidised bed technique for boilers. A fluidised bed exhibits excellent mass and heat transfer characteristics. This greatly increases the heat transfer to tubes immersed within the bed, thus leading to more compact equipment compared to conventional boilers. This mixing also promotes a homogeneous and relatively low temperature throughout the equipment, thus typical NO_x emission concentrations are very low. One other advantage of the technique, which is the focus of the current work, is that limestone can be injected directly into the bed, which acts as a sorbent for SO₂ produced during the combustion of fossil fuels. This is further expanded upon below. The limestone (which is

primarily calcium carbonate) injected into the bed thermally decomposes via



(1)

which produces calcium oxide, the active sorbent. The typical temperatures within FBC are high enough and the carbon dioxide concentration low enough for rapid decomposition of calcium carbonate. As a result the initially reaction is not thought of as a limiting step in the overall process (Stauer et al., 1989. and Mulligan. et al. 1989). The next stage of the process is the adsorption of the SO_2 , which proceeds according to:



The CSFB or Comprehensive Simulator for Fluidised Bed (de Souza-Santos 1987, 1989 and 1994) has been developed. The code has been validated against experimental data and been shown to be capable of predicting many key variables of the bed and freeboard, including, detailed temperature and concentration profiles, fluidisation parameters and for the case of boilers the heat transfer rate to tubes immersed in the bed. Such a tool has proved to be valuable tool for the optimisation of equipment design, operating parameters and heat exchanger design and position. However, it has been shown that the sulphur capture model currently used in the code is not able to predict rates of sulphur capture for all cases. The objectives of the current work were to develop a sulphur capture model, which is able to predict sulphur capture efficiencies under all conditions.

2. SULPHUR CAPTURE MODELS

In 1970, it was first shown that the internal structure of calcined limestone participates in the sulphurisation reaction. Prior to this, it was assumed that only the outer surface was active. Since this realisation, models have been developed which incorporate features of the internal structure in an effort to predict the sorbent capabilities. The various models can be subdivided into three main categories, i) grain models, ii) pore models and iii) network models. Of the three the grain model has shown the greatest degree of success, particularly when experimental data regarding the limestone is known. The derived models exhibit a large diversity of complexity. The traditional approach in both the grain model and random pore model is to balance the bulk diffusion of a reactant gas through a porous medium with the chemical reactions on the interior surface area. The rate of diffusion into the solid is calculated utilising the effective diffusion coefficient, calculated from:

$$D_E = D\epsilon\tau^{-1} \quad (3)$$

where D_E is the effective diffusivity, D is the binary gas diffusion co-efficient, ϵ is the void fraction within the solid matrix and τ is the tortuosity. As the product has a larger volume than the reactant the porosity of the porous matrix is reduced as the reaction proceeds. This acts to reduce the rate of diffusion into the particle.

Initially the rate of reaction is kinetically controlled. As the reaction proceeds, an ionic product layer forms around the unreacted calcium oxide. After a certain conversion the reaction becomes limited by the rate that ions from the unreacted core can diffuse to the surface of the product layer where it reacts with sulphur containing gaseous compounds. The rate at which this diffusion occurs is typically one of the factors adjusted in order to match model predictions to experimental data. A review of tortuosity-porosity and values of product layer diffusion coefficient utilised within sulphur capture models is shown below.

2.1 Product Layer Diffusion Coefficient

The various values found in the literature are presented at Table 1.

Table 1. Value of the product layer diffusion-coefficient at 1123 K

Used in the Model of:	Model Type	Product layer diffusion coefficient, 1123 K (m ² /s)
Bhatia et al. 1981	Random Pore Model	2x10 ⁻¹²
Hartman et al. 1976	Grain Model	6x10 ⁻¹³
Dam-Johansen et al.1991	Grain Micro-Grain Model	2x10 ⁻¹¹
Alvfors et al. 1988	Pore Branching Model	1x10 ⁻¹²

The value of this variable varies over a factor of thirty in order to match experimental data to that predicted by the model.

2.2 Tortuosity Factor

The tortuosity factor is used to relate the gas binary diffusion coefficient to the effective rate of diffusion in a porous matrix of porosity ϵ is equated using Eq. 3. The various correlations used to estimate the tortuosity factors are shown in Table 2 below. As can be seen, the value of the effective diffusivity into the particle used in the models varies by a factor of three when ϵ equals 0.5. To help understand why such large variations of the magnitude of these two variables are required to match experimental and predicted data an investigation into the possible reasons has been conducted. The findings are outlined below.

Table 2. Value of the tortuosity factor used in Sulphur Capture Models

Used in the model of:	Taken from the work of:	Tortuosity Factor	D _E . for $\epsilon=0.5$
Alvfors et al. 1988	Assumed	1	D _E =0.5D
Hartman et al. 1976	Campbell et al. 1972	1.5	D _E =0.33D
Dam-Johansen et al.1991	Estimated. From concentration profiles.	3	D _E =0.166D
Bhatia et al. 1981	Wakoa et al. 1962	1/ ϵ	D _E =0.25D
Lin et al. 1993	Elias-Kohav et al. 1991	1/ $\epsilon^{0.65}$	D _E =0.318D

2.3 Associated Compounds

Within limestone some associated compounds are found. Typically these are compounds containing Si, Fe, Al, K, S and Sr. Some effects due to these compounds have been quantified and are described below.

Sintering is the mechanism by which solid particles coalesce when heated to temperatures below their melting points. The extent to which sintering occurs depends upon the temperature to which the particle is heated and to the surrounding gas composition and associated ionic compounds (Davini et al. 1991, Borgwardt 1981, Borgwardt 1989, Borgwardt 1970). During sintering, the typical effects are enlargement of the average pore radius coupled with a reduction of the internal BET surface area. At temperatures inherent within FBC, negligible changes in porosity occur (Davini et al. 1991).

It has been found that small quantities of Fe₂O₃ can effectively catalyse the sulphation reaction (Desel et al. 1983). Studies have been conducted where limestone particles have been

impregnated or the surface coated with iron oxide. In all cases the initial reaction was increased. The mechanism of the catalysis is not yet fully understood, nor has the magnitude of the increase in reaction rate been measured as a function of the Fe₂O₃ concentration.

2.4 Variations in the Physical Structure of Limestone

Naturally occurring limestones differ greatly in both physical structure and associated impurities. Physical structures change from the softer chalk species characterised by their low crushing strength (Spitsbergen et al. 1981) to the hard rock types. It has been proposed that the most accurate way to distinguish between different limestones is to categorise according to the geographical age, as shown below.

Geographically old limestone is typified by their hard crushing strength and high apparent density. The porosity of such stones is around two percent (SEMP Reprints Series 1991, Choquette et al. 1970, Tucker et al. 1990). Scanning Electron Microscope (SEM) photographs of such stones show an almost smooth surface with very few flaws. Geographically young limestone is typified by their low crushing strength and low apparent density. The maximum porosity of such stones is around fifty five percent for very young stones (SEMP Reprints Series 1991, Choquette et al. 1970, Tucker et al. 1990). SEM photographs of such stones reveals a very open and porous surface. The particle is made up of very small compact crystallites. The sizes of the crystallites within the softer limestones are usually much smaller than that of the hard rock types.

3. THEORY

The un-reacted core model is not directly applicable to express the rate of reaction between calcined limestone and sulphur dioxide. In the model it is assumed that a reaction front moves towards the centre of the particle, directly behind the front only products exist whilst directly in front only reactants exist. However, as will be described later, it is possible to derive scaling laws that adjust the reaction rate in order to account for the still reacting shell. A technique has been derived which avoids the need of assuming a value for the rate of diffusion through the product layer and is also described.

The assumptions made are:

1. The temperature is uniform throughout the stone.
1. The SO₂ must first diffuse through the boundary layer surrounding the particle, then diffuse through the reacted shell and then must diffuse into the unreacted core, before reaction takes place.

For this case the average rate of reaction of the particle is calculated by (de Souza-Santos, 1994)

$$r = \frac{1}{r_p} \frac{C_G - C_E}{\sum_{k=1}^3 U_{U,k}} \quad (4)$$

r is the rate of chemical reaction, [kmol/m² (of particle surface) s], r_p is the radius of the particle (m), C_G is the bulk gas concentration (Pa), C_E is the equilibrium gas concentration (Pa).

$U_{U,1}$ is the mass transfer resistance due to the boundary layer, calculated from

$$U_{U,1} = \frac{1}{N_{sh} D}$$

$U_{U,2}$ is the resistance due to the reacted shell, calculated from

$$U_{U,2} = \frac{1-a}{aD_s}$$

$U_{U,3}$ is the resistance due to the core combined with the kinetics, calculated from

$$U_{U,3} = \frac{1}{aD_c[a\Phi \coth(a\Phi) - 1]}$$

where N_{Sh} is the Sherwood Number, D is the molecular diffusion coefficient (m^2/s) in the gas layer, a is ratio between the radius of the unreacted part of the particle and the radius of the particle, D_s and D_c are the effective diffusivities in the shell and core respectively (m^2/s), Φ is the particle Thiele modulus. In order to calculate the reaction rate from Eq. (4), three factors, namely, ' k ', ' D_e ' and ' a ' must be calculated. The technique used to estimate these three factors is shown below.

3.1 Calculation of the rate of chemical reaction 'K'.

Borgwardt et al. (1986) studied the sulphation reaction within a differential reactor over the temperature range 800 - 1125 °C. To overcome boundary layer resistance, high gas flows were utilised whilst to minimise pore diffusion resistance the experiments were conducted with 1 μm diameter particles of precalcined calcium carbonate. From the findings of the work the following mechanism was proposed.

- 1) $SO_2 + \frac{1}{2}O_2 = SO_3$
- 2) $CaO = Ca^{2+} + O^{2-}$
- 3) O^{2-} diffuses to product layer surface
- 4) $SO_3 + O^{2-} = SO_4^{2-}$
- 5) $Ca^{2+} + SO_4^{2-} = CaSO_4$.

By a least-squared fit analysis the rate was deduced to be:

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = k_d t$$

where X is the conversion (atom S per atom Ca), t is time (s). k_d (1/s) is a diffusion constant, calculated from

$$k_d = 2.65 \times 10^{-6} S_g^2 P_{SO_2}^{0.62} \exp\left(-\frac{1.8426 \times 10^4}{T}\right) \quad (5)$$

where S_g is the internal specific surface area of calcine (m^2/kg), p_{SO_2} is the partial pressure of SO_2 in the bulk gas (Pa) and T is the temperature (K) of the bulk gas. The internal surface area is calculated using the expression derived by Rajan et al. (1980), shown below:

$$S_g = -3.843T + 5640 \quad \text{for } T \leq 1253 \text{ K} \quad (6)$$

$$S_g = 3.590T - 3670 \quad \text{for } T > 1253 \text{ K} \quad (7)$$

Using Eq. (5) the time to achieve the average conversion of the particle is calculated (t_1) along with the time for it to react a further 1% (t_2). This is the rate of change of the fractional conversion of the particle. The kinetic rate constant K is then related to this rate via:

$$\left(\frac{1.01X - X}{t_2 - t_1}\right) = \frac{m_p}{m_c} P_{SO_2} K \quad (8)$$

where X is the average conversion fraction, m_c is the mass change when 56 kg (1 kmol) of CaO is converted to 136 kg (1 kmol) of $CaSO_4$, m_p is the mass of an average calcined limestone particle prior to reaction, P_{SO_2} is the partial pressure SO_2 (Pa) in the bulk gas and K is the kinetic rate constant ($Pa^{-1} s^{-1}$). Equation 8 allows the rate constant to be calculated whilst avoiding the need to estimate the rate of diffusion through the ionic product layer.

3.2 Estimation of the Fraction of the Core which is Un-Reacted.

Through comparison of diffusion and reaction timescales it has been found that the ratio of kinetic to diffusion controlling effects, which define the reaction profile within the particle can be expressed as a modified Thiele modulus.

$$\Phi' = \left(\frac{KS_M C_{SO_2}}{D_{SO_2}} \right)^{0.5} \quad (9)$$

where K is the kinetic constant of the sulphation reaction (m/s), S_m is the internal surface area ($m^2/kmol$), C_{SO_2} is the concentration of SO_2 ($kmol/m^3$) and D_{SO_2} is the binary diffusion coefficient of SO_2 (m^2/s). The technique is illustrated using the data and parameter values derived by Hartman et al. (1976), the results are shown in the Figure below. In each case the solid line represents the experimental data and the dashed a line of gradient predicted by Eq. (9).

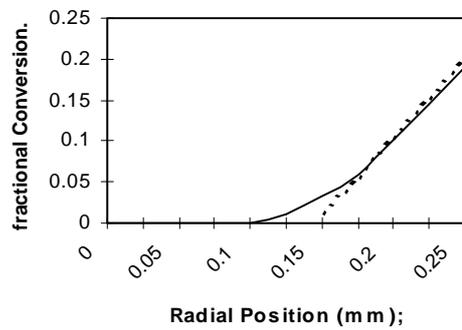


Figure 1. Comparison Between Experimental and Estimated Conversions as a Function of Radial Position

In Fig. 1: $K=6.6 \times 10^{-2}$ m/s, $S_m = 3 \times 10^5$ $m^2/kmol$, $C_{SO_2} = 1.43 \times 10^{-2}$ $kmol/m^3$, $D_{SO_2} = 7.5 \times 10^{-6}$ m^2/s .

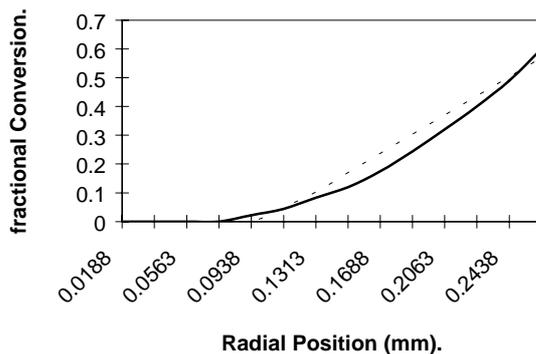


Figure 2. Comparison between experimental and estimated conversions as a function of radial position

In Fig. 2: $K=6.6 \times 10^{-2}$ m/s, $S_m = 3 \times 10^5$ $m^2/kmol$, $C_{SO_2} = 3.2 \times 10^{-2}$ $kmol/m^3$, $D_{SO_2} = 5 \times 10^{-6}$ m^2/s .

It must be emphasised that this technique is only an approximation as it has already been shown that the process is far more complicated than the simple approach taken here. However, as can be seen by the closeness of the two lines a reasonable approximation is made. To implement

this observation the following approach was taken. Firstly, it was assumed that the overall conversion of the particle could be related to the overall conversion of the shell by

$$\bar{X} = \frac{X_{RAV} V_S}{Z R_P^3} \quad (10)$$

where the right side is the average conversion of the particle, X_{RAV} is the average conversion in the shell, V_S is the volume of the reacted shell (m^3), Z is a constant equal to $4\pi/3$ and R_P is the radius of the particle (m). The position of X_{RAV} is defined as the position where the local conversion there is the average of the shell and computed by

$$X_{RAV} = (R_{AV} - R_C) \Phi' \quad (11)$$

where R_{RAV} is the position of average conversion within the particle, R_C is the radial position of the core of the particle (m), Φ' (m^{-1}) is the gradient of the conversion with respect to radial position calculated using Eq. (9). The position of average conversion within the shell is computed using

$$R_{AV} = \left(\frac{V_{RAV}}{Z} \right)^{1/3} \quad (12)$$

where V_{RAV} is the volume of a sphere of radius R_{AV} . The volume of the sphere of radius R_{AV} is defined as the volume of the core plus half the volume of the shell computed from

$$V_{RAV} = Z R_C^3 + \frac{V_S}{2} \quad (13)$$

and the volume of the shell calculated from

$$V_S = Z(R_P^3 - R_C^3) \quad (14)$$

The above equations are simplified by inserting Eq. (14) into (13), (13) into (12), (12) into (11) and (11) into (10). By defining y as the fraction of the radius of the particle occupied by the unreacted core i.e. $R_C = a R_P$, yields

$$\frac{\bar{X}}{\Phi' R_P} = \frac{(1 - y^3)(1 + y^3)^{1/3}}{2^{1/3}} - (1 - y^3)y \quad (15)$$

Within the simulation program, Eq. (15) is solved by an iterative method, to yield 'a'.

3.3 Calculation of the Effective Diffusivity D_e

The effective diffusivity of sulphur dioxide, through the shell and core, is calculated using Eq. (3). The tortuosity-porosity relationship developed by Elias-Kohav et al. (54) was used to scale the tortuosity to the porosity via:

$$\tau = \frac{1}{\epsilon^{0.65}} \quad (16)$$

yielding

$$D_E = D \epsilon^{1.65} \quad (17)$$

The porosity within the shell is calculated using the average conversion within the shell from Eq. (11), whilst the core porosity is calculated assuming complete calcination.

3.4 The Comprehensive Fluidised Bed Simulation Code

The CSFB code has been shown to be capable of simulating both combustion and gasification based processes. The code solves 42 differential equations, each as a function of the height above the distributor plate. A full description of the code and the validation cases can be found elsewhere and so will not be given here. The code generates detailed results regarding

concentration and temperature profiles, bubble diameters and composition, external heat rate losses, heat transfer to the tubes in the bed and freeboard, entrainment and elutriation rates of particles, fluidisation parameters and combustion efficiencies. The sulphur capture model has been implemented into the code and validated against four sets of experimental data. The results are given below.

4. RESULTS

The first validation case was performed by comparing simulation results with those measured by Babcock and Wilcox (1978), using a pilot scale fluidised bed combustor. A full description of the combustor and operating conditions can be found elsewhere (Babcock and Wilcox, 1978 and de Souza-Santos, 1987, 89) and so will not be given here. A comparison of the experimental and simulated results can be seen in Table 3.

Table 3. A Comparison of Experimental and Computed Results for The Babcock and Wilcox Pilot FBC.

Variable.	Experimental Results.	Simulation Results.
Temperature (Bed middle) K	1108	1209
Temperature (outlet) K	923	1074
Outlet SO ₂ . Mol% D.B.	0.08	0.0762
Ca:S Ratio in bed	2.2	2.2
Ca conversion %	28.09	25.4

As can be seen the experimental and simulation results compare very well. Further comparisons dealing with factors to which sulphur capture rates are not sensitive can be found elsewhere (de Souza-Santos 1987, 89).

Three further validation cases have been performed by comparing simulation results with those measured by the National Coal Board (NCB), England. The operating conditions for the three tests in which sulphur parameters were collected are shown in Table 4 below.

Table 4. Operating Conditions.

Variable.	NCB Test 3	NCB Test 5	NCB Test 7
Coal Flowrate.(g/s)	5.0	6.6	6.4
Limestone Flowrate (g/s).	1.75	2.25	3
Air flowrate.(g/s)	45	67	63
Recycle Ratio	1	1	0
Bed Height (m)	0.5	0.7	0.6

The model was found to greatly under predict the rate of sulphur capture for all cases. Analysis of the simulation results revealed that the major factor leading to the under prediction was due to bed separation. The majority of the limestone was present at the bottom of the bed with the coal burning above. A comparison of the Minimum Fluidisation Velocity (MFV) for the average diameters of coal and limestone found that the limestone required a velocity of over a factor of two higher. Under operating conditions it is normal to scale the average diameters to approximately match the MFV. However, during the tests the density of the coal was measured which allows the MFV of the coal to be calculated. The initial porosity of the limestone then took an assumed value in order to match the MFV of the limestone to that of the coal. It was found

that in order to match the MFV the limestone would have to be initially porous with a void fraction of 0.5. Tests using such a limestones have been completed (Dam-Johansen et al., 1991), who found that limestones having a void fraction of 0.5 prior to calcination typically develop an inner surface area of the order of 20 m²/g during calcination. The simulations where repeated using these values to represent the structure of the limestone used. A comparison of the experimental and simulated results is shown in Table 5.

Table 5. A comparison of experimental and computed results, National Coal Board FBC. Tests 3, 5 and 6.

Variable.	Test 3		Test5		Test6	
	Experim.	Simulation	Experim.	Simulation	Experim.	Simulation
Temperature (Bed middle) K	1123	1209	1123	1168	1120	1214
Temperature (outlet) K	1160	1112	1153	1125	1144	1156
Outlet SO ₂ . Mol% D.B.	0.0477	0.0423	0.0305	0.0387	0.0408	0.0413
Ca:S Ratio in Bed	2.75	2.75	2.5	2.5	4.2	4.2
Ca conversion %	Not available	30.9	Not available	32.34	Not available	20.2

As can be seen, by applying the assumption that the limestone used in tests was of a structure comparable to that of a young limestone the model has the ability to predict the rates of sulphur capture within the combustor.

5. CONCLUSIONS

The model has been shown to be capable of predicting rates of sulphur capture within FBC's. It is unfortunate that some of the variables required within the model had to take assumed values. However, there is clear evidence that the two limestones used in the different test must have considerable different reactivates. The average diameter of limestone used in the Babcock and Wilcox test is approximately half of that used in the NCB tests, whilst the residence time is twice as long. The temperature and Ca:S ratio are the same as is bed temperature and the overall conversion. This evidence strongly implies that the limestone was much less reactive than that used by the NCB. Assuming the NCB limestone was of a structure resembling young limestone greatly improved the simulation results for both bed characteristics and sulphur capture efficiencies.

The next step would be to verify the results through controlled experiments, in which the properties of the limestone are determined in order to set the correct parameters into the model.

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7. ACKNOWLEDGEMENTS

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