ELSEVIER

Chemical Engineering Journal 107 (2005) 119–125

Chemical Engineering Journal

www.elsevier.com/locate/cej

Modelling of in-duct desulfurization reactors

A. Garea*, J.A. Marques, A. Irabien

Dpto. Ingeniería Química y Química Inorgánica, ETSII y T., Universidad de Cantabria, ETSIIT, Avda. de los Castros s/n 39005 Santander, Spain

Abstract

The modelling of the in-duct desulfurization process at low temperatures was performed from data obtained in an entrained flow reactor at laboratory scale. Two modelling approaches were used for the process description under in-duct conditions in the reactor: (i) the application of the grain model to a single particle along the reactor, and (ii) a non-ideal adsorption equation for the gas–solid kinetics in order to solve the mass balances at a macroscopic level. It was used a synthetic flue gas stream with the typical composition of the coal-power plants, and the solid sorbent was commercial $Ca(OH)_2$. The experimental planning included the analysis of variables: calcium to sulfur molar ratio, SO_2 inlet concentration, temperature, relative humidity, residence time, and CO_2 presence in the gas stream. The experimental facility provided the measurement of SO_2 concentration in the gas phase along the reactor up to 4 s of residence time for gas and solid phases. The sensitivity analysis of variables was performed by the use of a neural network (MLP 6:4:1) where the target was the experimental SO_2 concentration along the reactor.

Keywords: Modelling; Entrained flow reactor; Gas-solid reaction; Shrinking core/grain; Non-ideal adsorption

1. Introduction

Related to the control of acid rain, new regulations must be taken into account to control the emission of SO_2 and NO_x. A simple, gas–solid technology to be applied to sulfur dioxide control in power plants is based on the injection of a basic reagent, mainly calcium hydroxide, in the duct in order to capture the pollutants. The use of commercial $Ca(OH)_2$ is widely reported because of its low cost, despite of its relatively low utilization level that can be increased by the use of additives or the recycling of the partially reacted sorbent from the particulate collection system.

The kinetic modelling of the gas–solid reaction between SO_2 and calcitic sorbents at microscopic level was reported in the literature from the basis of the shrinking core model as well as the grain model in order to describe the experimental results obtained from fixed bed or thermobalance systems at laboratory scale [1–3]. An attempt to the modelling of the desulfurization process under in-duct conditions from the basis of the grain model is reported by Garea et al. [4], working with data obtained at different calcium to sulfur molar ratios (Ca/S) in a flow reactor system.

The kinetic modelling of the desulfurization reaction was also described by Irabien et al. [5] from considering the adsorption of SO_2 on a non-ideal solid surface as the rate-controlling step of the reaction mechanism. The relevant decrease of the reaction rate with the solid conversion observed from experimental data, related to the interactions between SO_2 and the sorbent particles in the presence of water vapour, was described by an exponential dependence of the solid conversion [5–7], or a potential dependence reported with calcitic sorbents from recycling [8].

Two different assumptions for the description of surface heterogeneity were proposed from the several investigations focused on adsorption and reaction kinetics in catalysis: either surface sites non-identical or a mutual influence of adsorbed species.

The interaction phenomena was described by Murzin [9] in a surface electronic gas model which describes the non-homogeneity of the sorbent surface by adsorption–desorption equations where reaction rate dependences are also exponential with respect to the surface coverage. An overview of the kinetic modelling from adsorption mechanisms is reported by Garea et al. [6].

---

* Corresponding author. Tel.: +34 942 20 15 88; fax: +34 942 20 15 91.
E-mail address: gareaa@unican.es (A. Garea).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.12.018

Nomenclature

A	fitting parameter, Eq. (8) (s^{-1})
B	fitting parameter, Eq. (8), dimensionless
C^z SO_2	concentration in the gas phase at any axial position in the reactor ($mol\,m^{-3}$)
$d_{particle}$	particle diameter, mean value calculated from distribution (laser diffraction) (m)
D_{eg}	effective diffusivity of SO_2 in the grain ($m^2\,s^{-1}$)
D_{ep}	effective diffusivity of SO_2 in the particle ($m^2\,s^{-1}$)
k_s	surface reaction rate constant ($m\,s^{-1}$)
M_s	molecular weight of sorbent, $Ca(OH)_2$ ($g\,mol^{-1}$)
Q_g	gas flowrate = 0.43l s^{-1}
r	radial position in the particle (m)
r_{ads}	adsorption reaction rate, Eq. (11) (mol $m^{-2}\,s^{-1}$)
r_g	radial position of the unreacted core in the grain (m)
$r_{overall}$	overall reaction rate, Eq. (4) ($mol\,s^{-1}$)
R	radius of the particle = 2.75×10^{-6} m
R_g	radius of the grain = 8.64×10^{-8} m
S_e	BET specific surface area of the solid, calculated by BET fitting = 16 $m^2\,g^{-1}$
V_R	reactor volume = 1.26 l
x_g	local solid conversion for a grain, Eq. (5), dimensionless
x_s	overall solid conversion for the entire particle, Eq. (6), dimensionless
X^z	solid conversion in the gas phase along the axis of the reactor, dimensionless
Y^z	SO_2 dimensionless variable in the gas phase (related to the inlet molar fraction y_0) along the axis of the reactor (z)
Greek letters	
ε	porosity, dimensionless
ν	stoichiometric coefficient, dimensionless
ρ_s	solid molar density ($mol\,m^{-3}$)

The aim of this study is the modelling of the in-duct desulfurization reactors from data obtained in an entrained flow reactor under in-duct conditions. Two scopes of modelling were used: the grain model approach at a microscopic level applied to a single particle at any axial position along the reactor, and the adsorption process at a macroscopic level based on the non-ideal surface of the solid.

2. Experimental data

The prediction of the SO_2 removal efficiency was performed from data obtained in an entrained flow reactor at laboratory scale, which is described elsewhere [10,11]. The experimental facility is shown in Fig. 1.

Taking into account that the use of commercial grade $Ca(OH)_2$ is very important for practical applications of the desulfurization process in industry, the commercial grade solid available from supplier (lime industry: Calcinor S.A.) was selected for this study. The particle size distribution was measured by laser diffraction, with an average particle diameter of 5.5 μm.

The flow reactor (1 m length, 4 cm internal diameter) was provided by gas phase sampling points for the measurement of SO_2 concentration in the gas phase at different residence times in the reactor (Fig. 2).

The residence time was calculated as the volume at different length points along the reactor divided by flow rate of gas (STP). The volume was variable, calculated as the product of the reactor section and the variable length (corresponding to the sampling points along the reactor). The experiments were operated with constant flow rate of gas, 0.43 l s^{-1} (STP).

The SO_2 concentration in the gas phase at different residence times during an experiment was obtained from the sampling points along the reactor.

The operational parameters of the in-duct injection process are the calcium to sulfur molar ratio (Ca/S), and the residence time that determines the contact period between gas and solid phases in the flow reactor (or duct). Pilot plant data covered the intervals of Ca/S 1.5–18 (molar basis) and residence times 0.3–4 s. The influence of other variables in the gas–solid reaction was also considered in the experimental planning: relative humidity 50–70%, SO_2 inlet concentration 1000–2000 ppmv, temperature 50–70 °C, and CO_2 presence in the gas phase 0–12%.

3. Sensitivity analysis of variables

The sensitivity analysis of the considered variables in the SO_2 removal efficiency of the desulfurization process was performed by using a neural network approach as a non-linear fitting. A multi layer Perceptron network was configured as a MLP 6:4:1, including an input layer of six neurons, a hidden layer of four neurons, and an output layer with one neuron and a target value. The elements of the input layer are the variables: Ca/S molar ratio, residence time, relative humidity, SO_2 inlet concentration, temperature, and CO_2 content in the gas phase. The target value is the experimental dimensionless SO_2 concentration in the gas phase at any axial position along the reactor, related to the inlet concentration.

A total of 288 data points were introduced to the neural network analysis, divided in the training phase (142 data points as training set and 71 as verification set), and the test of the prediction capability (71 data points).

The training algorithm was the backpropagation, with values of 0.1 for the learning coefficient and the momentum correction factor, and 10,000 iterations over the training set for stabilising the weights in the trained architecture.

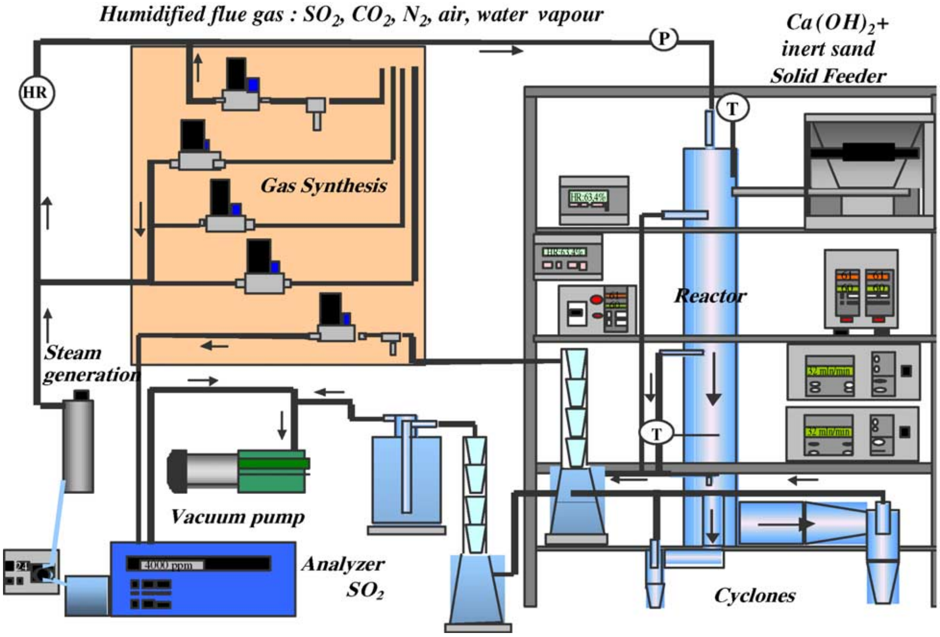

Fig. 1. Experimental facility. In-duct Injection system: flow reactor.

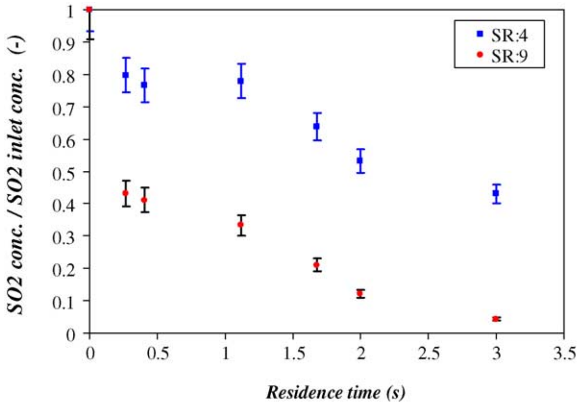

Fig. 2. Experimental trends of SO_2 concentration in the gas phase along the reactor. Ca/S molar ratios (SR) = 4, 9; 1000 ppmv SO_2, 12% CO_2, 60 °C, 60% relative humidity.

The global standard deviation of the predicted values of SO_2 dimensionless concentration related to the experimental ones was 0.081, with the correlation coefficients for data fitting: 0.948 (training set), 0.943 (verification set) and 0.873 (test set).

The results of the sensitivity analysis of variables are given in Table 1 in terms of the following parameters for each variable: the error that indicates the performance of the network if that variable is not taken into account, the ratio calculated dividing the error and the baseline error, and the rank which is the order of importance based in the descending error.

It is observed from Table 1 that the relevant variables are ranked 1–3: residence time, Ca/S molar ratio and relative humidity, with a deterioration of the network performance higher than 10% in the cases of excluding each of these variables. The ratio values of the variables ranked 4–6 indicates that the error is close to the baseline error, with no significant influence in the SO_2 removal prediction under the studied intervals of these variables.

4. Modelling and simulation results

The modelling of the gas–solid reaction under in-duct conditions was performed from two approaches: (i) the influence

Table 1
Sensitivity analysis of variables introduced to the neural network 6:4:1

	Residence time	Ca/S molar ratio	Relative humidity	Temperature	SO_2 inlet conc.	CO_2 presence
T-rank	1	2	3	4	5	6
T-error	0.203	0.127	0.119	0.081	0.077	0.071
T-ratio	2.91	1.82	1.70	1.16	1.11	1.01
V-rank	1	3	2	4	5	6
V-error	0.190	0.128	0.139	0.086	0.080	0.074
V-ratio	2.54	1.71	1.85	1.15	1.07	0.98

T, training set; V, verification set; rank, order of importance (descending error); error, network performance if the variable is unavailable; ratio: error/baseline error.

of mass transfer and chemical reaction on the overall reaction rate in the shrinking core/grain model at a microscopic level, and (ii) the non-ideal adsorption at a macroscopic level.

The simulation results corresponding to the data sets of the relevant variables from the sensitivity analysis were discussed, Ca/S molar ratios (1.5–18), relative humidities (50–70%) with residence times up to 4 s, at given reaction conditions (60 °C, 1000 ppmv SO_2 concentration, 12% CO_2 in the gas phase).

4.1. *Grain modelling approach*

At a microscopic level, the modelling of the gas–solid reaction that takes place in the in-duct reactor was based on the application of the shrinking core/grain equations to any single particle at any axial position along the reactor with the corresponding boundary conditions. The assumptions of negligible dispersion and isothermal conditions in the reactor were considered for solving the model equations that can be expressed as:

- The mass balance in the particle located at any axial position (z) along the reactor

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2 D_{\mathrm{ep}}\frac{\mathrm{d}C^z}{\mathrm{d}r}\right] = \frac{3\,(1-\varepsilon)}{4\pi R_{\mathrm{g}}^3} r_{\mathrm{overall}} \qquad (1)$$

$$r = \mathrm{R}, \quad C^z = C_0^z; \quad \text{and } r = 0, \ \frac{\mathrm{d}C^z}{\mathrm{d}r} = 0 \qquad (2)$$

- The extent of reaction for a given grain, calculated from the shrinking r_{g} with time

$$-\frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{4}{3}\pi r_{\mathrm{g}}^3 \rho_{\mathrm{s}}\right] = \frac{\nu_{\mathrm{s}}}{\nu_{\mathrm{SO_2}}} r_{\mathrm{overall}}, \quad \text{with} \quad r_{\mathrm{g}} = R_{\mathrm{g}} \text{ at } t = 0 \qquad (3)$$

- The overall reaction rate included the terms of surface reaction and diffusional mass transfer resistance in the product layer of the grain

$$r_{\mathrm{overall}} = \frac{C^z}{1/4\pi r_{\mathrm{g}}^2 k_{\mathrm{s}} + (R_{\mathrm{g}} - r_{\mathrm{g}})/4\pi r_{\mathrm{g}} R_{\mathrm{g}}^3 \left(D_{\mathrm{eg}}/R_{\mathrm{g}}^2\right)} \qquad (4)$$

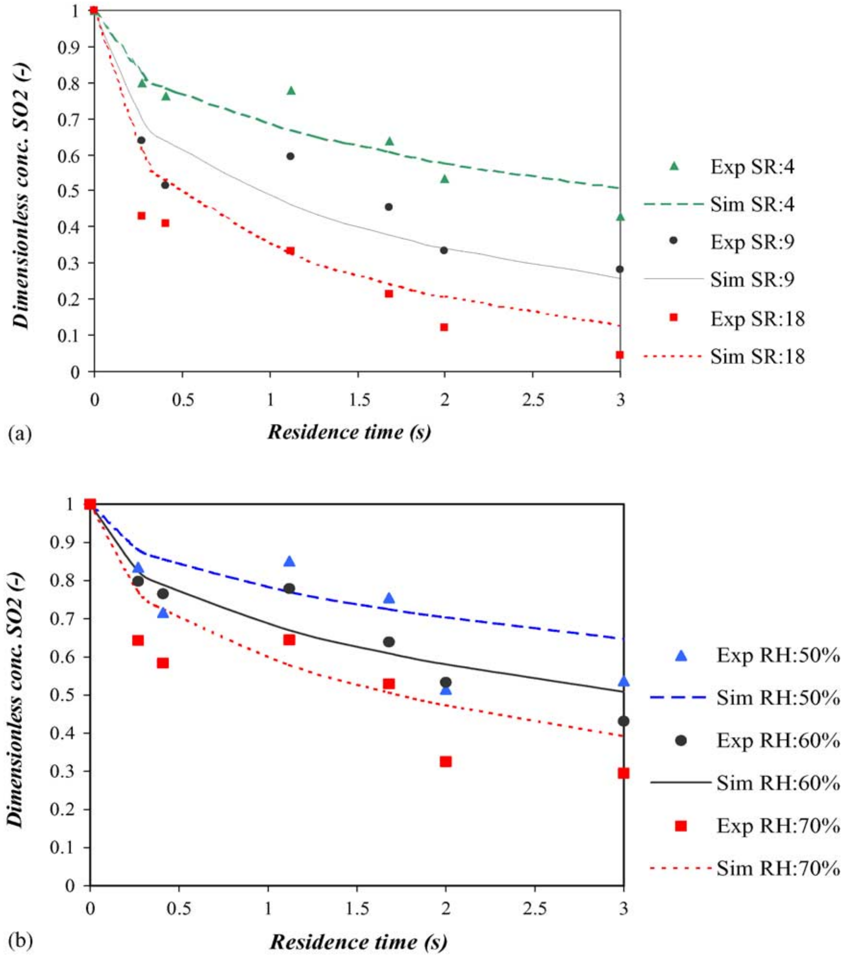

Fig. 3. Product layer diffusion results: experimental and simulated dimensionless concentrations of SO_2 at different Ca/S molar ratios (a) and relative humidities (b).

being considered negligible the intergrain mass transfer resistance, checked in previous studies [4].- The solid conversion, local and overall terms

$$x_g = 1 - \left(\frac{r_g}{R_g}\right)^3 \tag{5}$$

$$x_s = \frac{3\int_0^R x_g r^2 \, dr}{R^3} \tag{6}$$

- The simulated SO_2 concentration in the external gas phase at any axial position (C_0^z), which is related with the solid conversion by the material balance that includes the Ca/S molar ratio (SR):

$$C_0^z = (1 - x_s SR) C_{inlet} \tag{7}$$

The estimation of parameters, product layer diffusivity and kinetic constant, was based on the criteria of least square minimization related to the experimental data of SO_2 concentration in the gas phase along the reactor. It was used a commercial software, gPROMS (PSE Ltd.). The obtained results indicated that the controlling step is the diffusional resistance in the grain product layer. The dimensionless number *Damköhler II*, that accounts to the ratio of chemical reaction and diffusion rates, was established in 10^5, that implies a dimensionless SO_2 concentration at the surface in a negligible value.

The value obtained for the diffusional parameter, $(D_{eg}/R_g^2) = 657\, s^{-1}$ for the Ca/S data, that gives a product layer diffusivity in the order of $5 \times 10^{-12}\, m^2\, s^{-1}$, also indicates that the diffusion mechanism may be related to the SO_2 diffusion in the microporosity of grains. The influence of the relative humidity was introduced in the diffusional parameter (D_{eg}/R_g^2) in terms of an exponential function, taking into account that it is the conditioning variable for the solid utilization ability in the process as it was reported from previous works [7]. The fitting equation is given as

$$\left(\frac{D_{eg}}{R_g^2}\right) = A\, e^{B\,RH}, \text{ with RH\% and } \left(\frac{D_{eg}}{R_g^2}\right) \text{ in } s^{-1} \tag{8}$$

with the values of fitting parameters: $A = 3\, s^{-1}$; $B = 0.085$.

It was calculated the corresponding value of global standard deviation of the simulated SO_2 concentrations related to the experimental values, $\sigma_{n-1} = 0.124$, for the total number of experiments of the data series: Ca/S molar ratio, relative humidity and residence times.

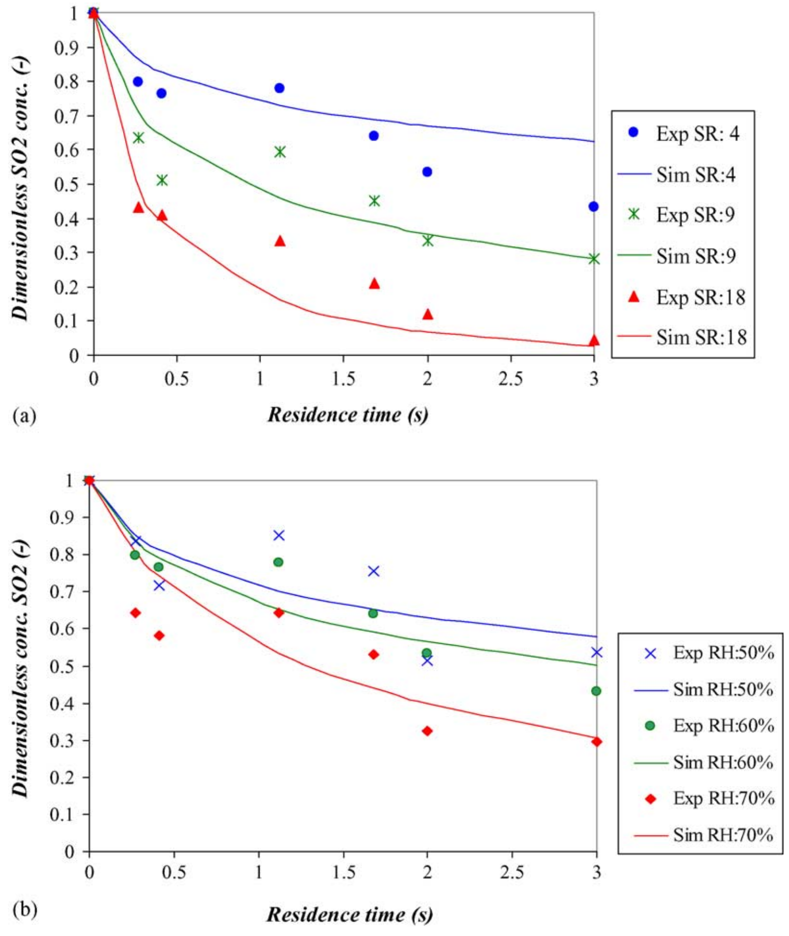

Fig. 4. Non-ideal adsorption results: experimental and simulated profiles of SO_2 dimensionless concentration at different Ca/S molar ratios (a) and relative humidities (b).

Some simulation results are shown in Fig. 3(a) different Ca/S with relative humidity at 60%, and (b) different relative humidities with Ca/S = 4.

4.2. Non-ideal adsorption modelling approach

At a macroscopic level, the modelling of the desulfurization process in the entrained flow reactor under isothermal conditions was described by the following equations:

- The mass balance of gas and solid phases along the reactor

$$\frac{V_R}{Q_g}\frac{\partial Y^z}{\partial t}+\frac{\partial Y^z}{\partial z}=-\frac{V_R}{Q_g}M_s S_e \,\mathrm{SR}\, r_{ads} \tag{9}$$

$$X^z=\frac{1-Y^z}{\mathrm{SR}} \tag{10}$$

  being Y^z the SO_2 dimensionless variable in the gas phase (related to the inlet molar fraction y_0) and X^z the corresponding solid conversion variable, along the axis of the reactor (z).
- The kinetic equation for sulfation, based on an adsorption process on a non-ideal solid surface, characterized by an exponential dependence of the solid conversion term in the reaction rate for describing the dramatic decrease observed from experimental data

$$r_s=k_s y_0 Y^z(1-X^z)\exp(-gX^z) \tag{11}$$

The estimation of the kinetic parameters (k_s and g) was performed by gPROMS, based on the criteria of least squares minimization related to the experimental data of SO_2 dimensionless concentration in the gas phase along the axial axis of the reactor (Y^z values). The solid conversion values (X^z) were also obtained from simulation.

The series of experiments corresponding to the Ca/S molar ratios, SR: 4–18, and relative humidity, RH: 50–70%, was described by the estimated parameters $k_s = 0.24$ (mol m^{-2} s^{-1}), and a variable g with RH that accounts to the non-ideal behaviour of the solid. From the simulation of the experiments at different relative humidities, it was observed that the parameter g decreases linearly at higher relative humidity, with the following fitting

$$g=65.8-0.84\,\mathrm{RH}(\%),\quad r^2=0.987 \tag{12}$$

Fig. 4(a) and (b) shows some simulation results of the experiments at Ca/S molar ratios (with 60% relative humidity) and relative humidities (with Ca/S = 4).

5. Conclusions

The sensitivity analysis of variables becomes relevant for the design and operation of the in-duct process. It was used as a neural network structure for the evaluation of the variables: Ca/S molar ratio, relative humidity, temperature, SO_2 inlet concentration, CO_2 presence in the gas phase, and residence time in the reactor. The sensitivity results remark the influences of the Ca/S molar ratio and the relative humidity at different residence times of gas and solid phases in the reactor for prediction of the SO_2 removal efficiency.

Taking into account the relevant variables, the process was described by two modelling approaches: (i) the SO_2 diffusion in the small grains of a moving particle, along the reactor, and (ii) the SO_2 adsorption on the surface of solid particles.

The correlation between the experimental and the predicted values of SO_2 concentration was calculated in both cases: (i) $\sigma_{n-1} = 0.13$, and (ii) $\sigma_{n-1} = 0.12$, It was required a variable parameter as a function of the relative humidity that accounts to the solid behaviour.

The results of the non-ideal adsorption kinetics in the mass balances of gas and solid phases provide a better prediction for lower values of dimensionless SO_2 concentrations that supposes higher SO_2 removal efficiencies along the reactor.

Acknowledgement

This research has been financially supported by Ministry of Science and Technology of Spain (Project No. PPQ2000-0251).

References

[1] A. Garea, J.L. Herrera, J.A. Marques, A. Irabien, Kinetics of dry flue gas desulfurization at low temperatures using $Ca(OH)_2$: competitive reactions of sulfation and carbonation, Chem. Eng. Sci. 56 (2001) 1387–1393.

[2] M. Maalmi, A. Varma, W.C. Strieder, The sharp interface model: zero-order reaction with volume change, Ind. Eng. Chem. Res. 34 (1995) 1114–1125.

[3] S.K. Mahuli, R. Agnihotri, R. Jadhav, S. Chauk, L.-S. Fan, Combined calcination, sintering and sulfation model for $CaCO_3$—SO_2 reaction, AIChE J. 45 (1999) 367–382.

[4] A. Garea, J.A. Marques, T.L. Hechavarría, A. Irabien, Simulation of the FGD in-duct injection technology using complex kinetic models, in: R. Gani, S.B. Jorgensen (Eds.), Proceedings of the European Symposium on Computer Aided Process Engineering, vol. 11, Elsevier, Amsterdam, pp. 147–152.

[5] A. Irabien, F. Cortabitarte, M.I. Ortiz, Kinetic model for desulfurization at low temperatures using calcium hydroxide, Chem. Eng. Sci. 47 (1992) 3427–3433.

[6] A. Garea, J.R. Viguri, A. Irabien, Kinetics of flue gas desulfurization at low temperatures: fly as/calcium (3/1) sorbent behaviour, Chem. Eng. Sci. 52 (1997) 715–732.

[7] A. Garea, J.L. Herrera, J.A. Marques, A. Irabien, Kinetics of dry flue gas desulfurization at low temperatures using $Ca(OH)_2$: competitive reactions of sulfation and carbonation, Chem. Eng. Sci. 56 (2001) 1387–1393.

[8] A. Kavouras, B. Breitschaedel, G. Krammer, A. Garea, J.A. Marques, A. Irabien, SO_2 removal in the filter cake of a jet-pulsed filter: a

combined filter and fixed-bed reaction model, Ind. Eng. Chem. Res. 41 (2002) 5459–5469.

[9] D.Y. Murzin, Modeling of adsorption and kinetics in catalysis over induced nonuniform surfaces, Ind. Eng. Chem. Res. 34 (1995) 1208–1218.

[10] J.A. Marques, A. Garea, A. Irabien, Proceedings of the 14th International Congress of Chemical and Process Engineering, CHISA, 2000, pp. 45, 1.

[11] J.A. Marques, A. Garea, A. Irabien, in: Proceedings of the 11th International Conference on Coal Science, DOE/NETL-2001/1153.