

# A single particle model of lime sulphation with a fractal formulation of product layer diffusion



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## HIGHLIGHTS

- A fractal-like formulation of the random pore model was proposed.
- Time-dependence of product layer diffusivity was accounted for.
- A link between product layer diffusivity and structural ordering was established.
- Time-decrease of diffusivity was related to reduced ions mobility in the lattice.
- Fluidized bed in situ desulphurization was investigated as case-study.

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## ABSTRACT

A fractal-like formulation of the random pore model (RPM) is proposed for the reaction of a gas with a solid, with the rate controlled by both diffusion in the layer of solid product and the kinetics of reaction. This approach gives a time-dependent diffusivity in the product. The model's predictions are compared with measurements of the removal of SO<sub>2</sub> with limestone, carried out in a lab-scale fluidized bed reactor. The fractal-like RPM described the production of CaSO<sub>4</sub> better than the standard RPM, which over-estimated the uptake of SO<sub>2</sub> in the first 40 min. The decrease of diffusivity in the product layer with time was ascribed to the degree of crystallization of the product, CaSO<sub>4</sub>, increasing with time and resulting in a lower ionic mobility in its lattice. The equation proposed is a simple and general one for a gas reacting with a solid (alternative example: the carbonation of lime), whose microstructural properties change significantly with the extent of reaction.

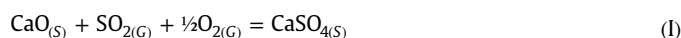
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## 1. Overview

Reactions of a solid sorbent with acid gaseous compounds (e.g., CO<sub>2</sub>, SO<sub>2</sub>) have long been studied in a variety of contexts, mostly related to environmental issues (Anthony and Granatstein, 2001; Boot-Handford et al., 2014; Cheng et al., 2003; Coppola et al., 2012, 2013; Montagnaro et al., 2002). Although modeling of these processes has advanced considerably, there are still some open issues associated with the proper consideration of intrinsic reaction kinetics, intraparticle diffusion in complex pore networks and diffusion in the product layer as they are influenced by the progress of reaction. Single particle modeling of these heterogeneous processes is a prerequisite to reliable design and operation of the

chemical converter.

In this study we will address SO<sub>2</sub> capture by a Ca-based sorbent. It is known that fluidized bed (FB) combustion of solid fuels takes advantage from the possibility of performing in situ desulphurization in the presence of cheap limestone-based sorbents (Hlincik and Buryan, 2013; Lyngfelt and Leckner, 1999; Montagnaro et al., 2010; Rozelle et al., 2007; Zhao et al., 2013). In particular, under operating conditions relevant to FB combustors (atmospheric pressure and temperatures around 800–900 °C), CaCO<sub>3</sub>, which is the largest constituent of the limestone, undergoes fast calcination to give porous CaO, which, in turn, is able to capture SO<sub>2</sub> – produced by combustion – in situ according to the sulphation reaction:



Reaction (1) is far from being complete, due to the complex

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## Nomenclature

$C_b$	SO <sub>2</sub> concentration [moles/volume]
$\mathcal{D}_e$	pore diffusivity [length <sup>2</sup> /time]
$\mathcal{D}_e^0$	initial pore diffusivity [length <sup>2</sup> /time]
$\mathcal{D}_p$	diffusivity in the product layer [length <sup>2</sup> /time]
$\mathcal{D}_p'$	value of the diffusivity in the product layer for $\theta=1$ [length <sup>2</sup> /time]
$h$	fractal exponent [–]
$k_s$	kinetic constant of sulphation [length <sup>4</sup> /(mole × time)]
$L_0$	total pore length per unit volume [1/length <sup>2</sup> ]
$M$	molecular weight of CaO [mass/mole]
$n$	exponent defined in Eq. (3) [–]
$R$	pore radius [length]
$R_{max}$	maximum value for pore radius [length]
$S_0$	pore surface area per unit volume [1/length]
$t$	actual reaction time [time]
$t^*$	characteristic time of reaction defined by Eq. (1-e) [time]

$x$	degree of Ca sulphation, reaction (1) [–]
$x_{max}$	maximum degree of Ca sulphation [–]
$V$	specific volume of pores [volume/mass]
$V_{tot}$	total specific volume of pores [volume/mass]

## Greek symbols

$\alpha_L$	molar volume of CaO [volume/mole]
$\alpha_S$	molar volume of CaSO <sub>4</sub> [volume/mole]
$\beta$	parameter defined by Eq. (1-b) [–]
$\epsilon_0$	particle porosity [–]
$\xi$	structural order parameter [–]
$\rho$	CaO density [mass/volume]
$\theta$	dimensionless time defined by Eq. (1-d) [–]
$\chi$	fractional degree of Ca sulphation [–]
$\psi$	structural parameter defined by Eq. (1-a) [–]
$Z$	ratio of volume of solid phase after/before reaction [–]

diffusive and kinetic phenomena involved in SO<sub>2</sub> capture by the sorbent. These phenomena have been modeled by several researchers (Allen and Hayhurst, 1996; Antonioni et al., 2016; Bhatia and Perlmutter, 1980, 1981a, 1981b; Borgwardt et al., 1987; Dam-Johansen and Østergaard, 1991a, 1991b; Duo et al., 2000, 2004; Hartman and Coughlin, 1976; Montagnaro et al., 2011; Takkinen et al., 2011). An example of investigation on the relationship between sorbent's conversion and reaction time through experimental and modeling activity is given by Dennis and Hayhurst (1986), where the blocking of pores following the course of sulphation is considered. The random pore model (RPM) proposed by Bhatia and Perlmutter (1980, 1981a, 1981b) has been widely adopted to describe the dynamic evolution of gas–solid reactions (Borgwardt et al., 1987; Duo et al., 2000, 2004; Stendardo and Foscolo, 2009). It accounts for the effect of pore structural parameters on both kinetic and diffusional mechanisms involved in the process. The rate-determining step of the desulphurization process depends on both reaction temperature and granulometry/pore size distribution of the CaO sorbent (Allen and Hayhurst, 1996; Borgwardt et al., 1987; Duo et al., 2000, 2004). Nonetheless, the diffusion of reactants through the growing product layer (CaSO<sub>4</sub>) usually governs the kinetics of SO<sub>2</sub> capture in the late stages of the process (Duo et al., 2000, 2004; Hartman and Coughlin, 1976). The characteristic diffusivity in the product layer is usually assumed invariant with the sorbent's conversion. Stendardo and Foscolo (2009) proposed a modified version of the RPM model for the carbonation of lime, in which the diffusivity in the product layer is a function of the sorbent's conversion to account for structural changes of the product shell with time. In this framework, Koppelman (1988) demonstrated that heterogeneous processes governed by diffusion exhibit rate coefficients dependent on time (fractal-like kinetics). Our research group has recently given a contribution to this topic, by validating the fractal approach for fluid–solid adsorption processes based on a time-dependent diffusion coefficient to account for segregation of chemical species taking place within the pore space of the sorbent (Balsamo and Montagnaro, 2015; Montagnaro and Balsamo, 2014). To the best of our knowledge, the adoption of theoretically-supported fractal-like kinetic concepts has not been reported for sulphation processes so far.

In this study a new fractal approach to the standard random pore model for gas–solid reactions with combined product diffusion and kinetic control is proposed. A fractal nature for the

diffusion coefficient in the product layer is introduced. The model has been applied to the case-study of in situ FB desulphurization, and its validation has been accomplished by taking into account experimental data reported in an earlier paper (Scala et al., 2008). The results have been critically discussed in the light of the main phenomena involved in the conversion process.

## 2. Experimental sulphation tests

The experimental data concerning the degree of Ca sulphation ( $x$ ) as a function of time  $t$  (at the temperature of 850 °C and atmospheric pressure) were taken from Scala et al. (2008). The operating conditions under which these data were obtained are briefly summarized here (the reader is referred to the cited paper for further information). Sulphation tests were carried out in a lab-scale FB reactor, electrically heated. The sorbent (0.4–0.6 mm size, batchwise fed to the reactor) was a limestone nearly pure in CaCO<sub>3</sub>, termed “limestone A” in the earlier manuscript. The inlet concentration of SO<sub>2</sub> in the model gas was set at the typical value of  $C_b = 1800 \text{ ppm} = 1.95 \times 10^{-5} \text{ kmol m}^{-3}$ . Fig. 1 shows the  $x(t)$  trend. The ultimate calcium conversion was  $x_{max} = 0.25$  after 120–

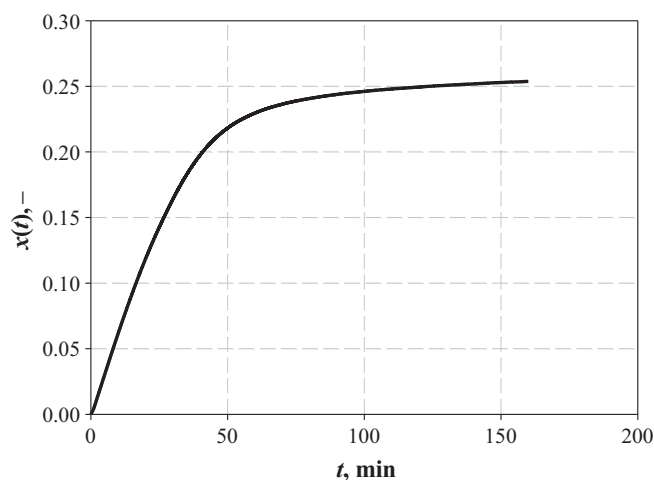


Fig. 1. Degree of calcium conversion as a function of time during the sulphation of limestone A (0.4–0.6 mm) at 850 °C in a lab-scale fluidized bed reactor (inlet concentration of SO<sub>2</sub> = 1800 ppm). Rearranged after Scala et al. (2008).

160 min sulphation, in line with typical values encountered for in situ FB desulphurization due to the plugging effect exerted by the  $\text{CaSO}_4$ -based shell to the unconverted core based on CaO.

### 3. The model

The reaction under investigation is sulphation of CaO (reaction 1) since, as recalled in the overview, limestone calcination to CaO occurs along time scales much shorter than those typical of the subsequent CaO sulphation. The starting equation comes from assuming the random pore model, with control by either diffusion in the product ( $\text{CaSO}_4$ ) or the kinetics of reaction (1). Here, the formulation proposed by Bhatia and Perlmutter (1981b; Eq. (27) of that paper) is adopted, by substituting  $x$  with the fractional conversion  $\chi = x/x_{\max}$ :

$$\chi = 1 - \exp \left\{ \frac{1}{\psi} - \frac{\left[ \sqrt{1 + \beta Z \theta} - \left( 1 - \frac{\beta Z}{\psi} \right) \right]^2}{\beta^2 Z^2} \right\} \quad (1)$$

In Eq. (1),  $\psi$  is a structural parameter defined as

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \quad (1-a)$$

where  $L_0$  is the total pore length per unit volume,  $\varepsilon_0$  is the porosity of the sorbent particle and  $S_0$  is the pore surface area per unit volume. The parameter  $\beta$  is expressed as

$$\beta = \frac{2k_S \rho(1-\varepsilon_0)}{M \mathcal{D}_p S_0} \quad (1-b)$$

where  $k_S$  is the kinetic constant,  $\rho$  and  $M$  are the CaO density and molecular weight, respectively, and  $\mathcal{D}_p$  is the diffusivity in the product ( $\text{CaSO}_4$ ).  $Z$  is the ratio of volume of solid phase after/before reaction:

$$Z = 1 + \frac{\rho \alpha_L \left( \frac{\alpha_S}{\alpha_L} - 1 \right)}{M} \quad (1-c)$$

where  $\alpha_S$  and  $\alpha_L$  are the molar volumes for sulphated Ca and lime (CaO), respectively. The dimensionless time  $\theta$  reads

$$\theta = \frac{t}{t^*} = \frac{k_S C_b S_0 t}{1-\varepsilon_0} \quad (1-d)$$

where the characteristic reaction time is:

$$t^* = \frac{1-\varepsilon_0}{k_S C_b S_0} \quad (1-e)$$

Mathematical manipulation of Eq. (1) concerning the fractional conversion  $\chi(t)$  leads to the equivalent form

$$\chi = 1 - \exp \left\{ \frac{1}{\psi} - \frac{\left[ \sqrt{1 + \frac{2k_S \rho C_b t}{M \mathcal{D}_p}} Z - \left( 1 - \frac{2k_S \rho(1-\varepsilon_0)Z}{M \mathcal{D}_p S_0} \right) \right]^2}{\left( \frac{2k_S \rho(1-\varepsilon_0)}{M \mathcal{D}_p S_0} \right)^2 Z^2} \right\} \quad (2)$$

Eq. (2) will be also referred to as “RPM-S”, to indicate the standard form of the random pore model.

A degree of structural reorganization ( $\xi \in [0; 1]$ ) is now introduced, which is a measure of the extent of crystallization of the product layer as sulphation proceeds. The parameter of structural order  $\xi$  is related to hindrance of reactants' diffusion in the

product layer (phenomenon highlighted, e.g., in Duo et al., 2004) by letting  $\mathcal{D}_p \propto (1-\xi)$ . Borrowing an approach developed by Salatiello et al. (1999) in the context of studies on the thermo-deactivation of coal char, the time-course of  $\xi$  has been related here to the sulphation kinetics according to

$$\frac{d\xi}{dt} = \frac{1}{t^*} (1-\xi)^n \quad (3)$$

where  $n$  is a reaction order, typically much larger than unity. Elaboration on Eq. (3) is reported in Appendix A, and yields  $(1-\xi) \propto \theta^{-h}$ , with  $h(n)$  expressed by Eq. (A-5). Therefore, the diffusivity of reactants in the product layer depends on the dimensionless time according to  $\mathcal{D}_p \propto \theta^{-h}$ . In the light of the present development, the fractal formulation of diffusivity in the product layer presented by Balsamo and Montagnaro (2015) is consistent with the  $n$ -th order kinetics of the time-course of the parameter of structural order expressed by Eq. (3). We now set

$$\mathcal{D}_p = \mathcal{D}'_p \theta^{-h} \equiv \frac{\mathcal{D}'_p}{(t^*)^{-h}} t^{-h} \quad (4)$$

where  $\mathcal{D}'_p$  is the value assumed by  $\mathcal{D}_p$  when  $\theta = 1$ . It is noteworthy that this relationship (see also Eq. (1-e)) agrees with findings reported in the literature (e.g., Duo et al., 2004 and papers reported therein) which show that the larger the concentration of  $\text{SO}_2$ , the lower is the diffusivity in the product. Due to the fractal nature of Eq. (4) in the time domain, it is valid for  $t \geq 1$  and for fractal exponent  $h \in [0; 1]$ . In particular, this last assumption means that (see Eq. (A-5))  $n \geq 2$ .

Therefore, introducing Eq. (4) – which reports the fractal-like formulation for the diffusivity in the product layer – into the RPM-S Eq. (2), this last is converted into its fractal (“RPM-F”) counterpart (which reduces to RPM-S if  $h=0$ ), as

$$\chi = 1 - \exp \left\{ \frac{1}{\psi} - \frac{\left[ \sqrt{1 + \frac{2k_S \rho C_b t^{1+h}}{M \mathcal{D}'_p (t^*)^h}} Z - \left( 1 - \frac{2k_S \rho(1-\varepsilon_0)Z}{M \mathcal{D}'_p (t^*)^h S_0} \right) \right]^2}{\left( \frac{2k_S \rho(1-\varepsilon_0)}{M \mathcal{D}'_p (t^*)^h S_0} \right)^2 Z^2} \right\} \quad (5)$$

Diffusion in the product layer limits the overall rate and overtakes diffusion inside the pores ( $\mathcal{D}_e$ ) as the rate-limiting step, as demonstrated by evaluating  $\mathcal{D}_e$  according to Bhatia and Perlmutter (1981a):

$$\mathcal{D}_e = \mathcal{D}_e^0 \left[ 1 - \frac{(Z-1)(1-\varepsilon_0)}{\varepsilon_0} \chi \right] \quad (6)$$

where  $\mathcal{D}_e^0$  is gas diffusivity in the unconverted porous solid.

### 4. Evaluation of model parameters

The parameters needed in the model are listed in Table 1 and were evaluated as follows. The porosimetric characterization for the calcined limestone reported in Scala et al. (2008) has been post-processed to give  $L_0$ ,  $S_0$  and  $\varepsilon_0$ , calculated according to Bahrami et al. (2014):

$$L_0 = \frac{1}{\pi \left( V_{\text{tot}} + \frac{1}{\rho} \right)} \int_0^{R_{\max}} \frac{dV}{R^2} dR \quad (7)$$

**Table 1**

Up: values of the main parameters of the random pore model obtained for limestone A sorbent. Down: values of other parameters.

$L_0$ [m <sup>-2</sup> ]	$S_0$ [m <sup>-1</sup> ]	$\varepsilon_0$ [-]	$\psi$ [-]	$Z$ [-]
$3.91 \times 10^{14}$	$3.41 \times 10^7$	0.42	2.45	3.11
$x_{\max}$ [-]	$\rho$ [kg m <sup>-3</sup> ]	$\alpha_L$ [m <sup>3</sup> kmol <sup>-1</sup> ]	$\alpha_S$ [m <sup>3</sup> kmol <sup>-1</sup> ]	$C_b$ [kmol m <sup>-3</sup> ]
0.25	3350	0.0169	0.0522	$1.95 \times 10^{-5}$
				$3.75 \times 10^{-4}$

$$S_0 = \frac{2}{V_{\text{tot}} + \frac{1}{\rho}} \int_0^{R_{\max}} \frac{dV}{R} dR \quad (8)$$

$$\varepsilon_0 = \frac{V_{\text{tot}}}{V_{\text{tot}} + \frac{1}{\rho}} \quad (9)$$

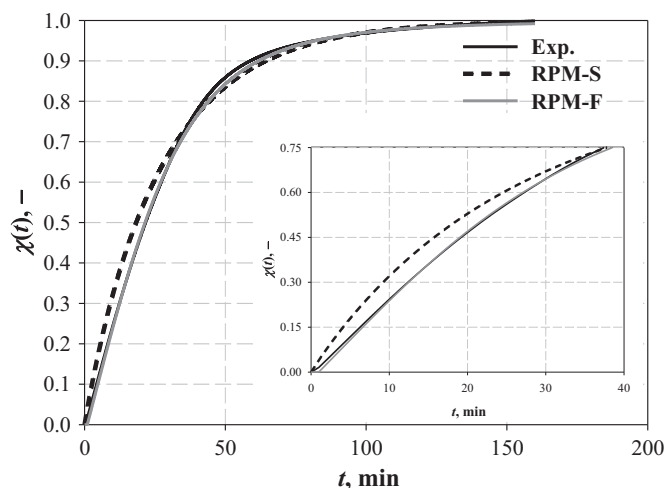
where  $V_{\text{tot}}$  is the total specific volume of pores in the size range investigated (up to  $R_{\max}=1000$  nm) and  $V$  is the specific volume for pores having radius  $R$ . By assuming  $\rho=3350$  kg m<sup>-3</sup> and having calculated  $V_{\text{tot}}=212.4$  mm<sup>3</sup> g<sup>-1</sup> for the calcine at hand, it is  $L_0=3.91 \times 10^{14}$  m<sup>-2</sup>,  $S_0=3.41 \times 10^7$  m<sup>-1</sup> and  $\varepsilon_0=0.42$ , values consistent with those reported in literature for similar sorbents (Bhatia and Perlmutter, 1981a). By using Eq. (1-a), the structural parameter is  $\psi=2.45$ . For the evaluation of the Z-ratio (Eq. (1-c)), it is assumed  $\alpha_L=0.0169$  m<sup>3</sup> kmol<sup>-1</sup> and  $\alpha_S=0.0522$  m<sup>3</sup> kmol<sup>-1</sup>. It is  $Z=3.11$  (cf. Borgwardt et al., 1987). Finally,  $\mathcal{D}_e^0$  has been estimated by considering its dependence on both porosity and Knudsen/molecular diffusivities following standard approaches. It results  $\mathcal{D}_e^0=3.75 \times 10^{-4}$  m<sup>2</sup> min<sup>-1</sup>.

## 5. Results and discussion

The assumption underlying the study is that the rate of conversion is subject to combined diffusion and chemical kinetic control (Section 3). This has been the result of preliminary investigation based on separate assessment of either the pure diffusive or pure kinetic control for both standard and fractal formulations. From a statistical regression analysis, the mixed control RPM was that showing the best behavior, and results from its application are reported here. The RPM-S (Eq. (2)) and the RPM-F (Eq. (5)) models were applied considering 2 ( $k_S$  and  $\mathcal{D}_p$ ) and 3 ( $k_S$ ,  $\mathcal{D}_p$  and  $h$ ) fitting parameters, respectively.

Experimental data of degree of Ca conversion shown in Fig. 1 have been reported again in Fig. 2, in terms of  $\chi(t)$  plot. The experimental trend of the fractional degree of calcium sulphation over time has been fitted using both RPM-S and RPM-F, as shown in Fig. 2, where a magnification of the results for short (< 40 min) reaction times is highlighted, too. For  $t > 40$  min both the standard and the fractal models fit well the experimental data (indeed, RPM-F resulted into a slightly better performance). For shorter sulphation times the fitting results show that RPM-S significantly overpredicts the experimental  $\chi(t)$ . On the other hand, the fractal approach proposed here behaves in a very satisfying way also for  $t < 40$  min.

From the quantitative point of view, the statistical regressions shown in Fig. 2 were those having the lowest possible value for the HYBRID function: 0.31 and 0.034 for the standard and the fractal case, respectively. Considering these cases (Table 2), the following best-fitting parameters were obtained: the kinetic constant of sulphation equals  $3.56 \times 10^{-5}$  and  $2.34 \times 10^{-5}$  m<sup>4</sup> kmol<sup>-1</sup> min<sup>-1</sup> for the standard and the fractal approach, respectively. The diffusivity in the product layer predicted by RPM-S is  $7.04 \times 10^{-11}$  m<sup>2</sup> min<sup>-1</sup>



**Fig. 2.** Fractional degree of calcium sulphation vs. time for limestone A sorbent. Comparison between experimental data (black line) and fitting with standard (RPM-S; black dashed line) and fractal-like (RPM-F; gray line) random pore models. The inset shows the kinetic patterns for short sulphation times.

**Table 2**

Fitting parameters obtained from standard and fractal-like random pore models.

RPM-S		
$k_S$	m <sup>4</sup> kmol <sup>-1</sup> min <sup>-1</sup>	$3.56 \times 10^{-5}$
$\mathcal{D}_p$	m <sup>2</sup> min <sup>-1</sup>	$7.04 \times 10^{-11}$
HYBRID	–	0.31
RPM-F		
$k_S$	m <sup>4</sup> kmol <sup>-1</sup> min <sup>-1</sup>	$2.34 \times 10^{-5}$
$\mathcal{D}_p$	m <sup>2</sup> min <sup>-1</sup>	$2.83 \times 10^{-10}$
$h$	–	0.91
HYBRID	–	0.034

(cf. Borgwardt et al., 1987), while the  $\mathcal{D}_p$ -value predicted by RPM-F is  $2.83 \times 10^{-10}$  m<sup>2</sup> min<sup>-1</sup> with  $h=0.91$ . This high value for the fractal exponent witnesses the intrinsic heterogeneous nature of the sorbent at hand, that determines a strong  $t$ -dependence for  $\mathcal{D}_p$  (see Eq. (4)).

Altogether, it is highlighted that the fractal random pore model better accounts for the time-dependence of the diffusivity in the product and, hence, kinetic and diffusive parameters.

Fig. 3 reports the time series of  $\mathcal{D}_p$  obtained through the fractal model Eq. (4).  $\mathcal{D}_e$  was calculated by using Eq. (6) where the experimental  $\chi(t)$  relationship has been introduced. First of all, it is observed that  $\mathcal{D}_e$  turns out to be several orders of magnitude larger than  $\mathcal{D}_p$ , a feature that further confirms the idea that the diffusivity in the product layer is the rate-limiting phenomenon for the process of SO<sub>2</sub> capture. Pore diffusivity decreases along

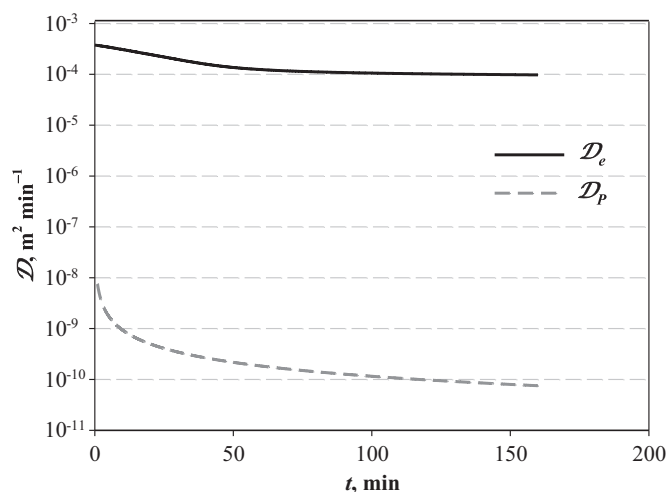


Fig. 3. Time evolution of the diffusivities in the product layer ( $D_p$ ) and in pores ( $D_e$ ).

with reaction time since sulphation brings about a closure of the accessible porosity of the particle, as experimentally verified in Scala et al. (2008). Diffusivity in the  $\text{CaSO}_4$  shell, when examined in the frame of the fractal theory, shows a stronger dependence on reaction time: actually, two orders of magnitude are lost for  $D_p$  from the beginning to the end of the reaction. This behavior could be related, in accordance to the fractal rate theory, to the segregation of the gaseous and solid reactants determined by the development of a layer of  $\text{CaSO}_4$  product that slows down the sulphation process (Kopelman, 1988; Scala et al., 2008). More specifically, the structure of the product shell changes along with sulphation due to the combined course of nucleation and crystallization (Duo et al., 2000, 2004). Once a continuous product layer has formed, the rate-governing mechanism, as proposed and experimentally verified by Hsia et al. (1993, 1995), would be an outward diffusion of ionic species. Accordingly,  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  ions diffuse outward through the  $\text{CaSO}_4$  layer from the  $\text{CaO}/\text{CaSO}_4$  interfaces, and the reaction with gaseous species occurs at the  $\text{CaSO}_4/\text{gas}$  interfaces. The diffusion rate in ionic solids mainly occurs by a vacancy mechanism and it increases with the increase in concentration of lattice defects (Borgwardt et al., 1987; Mehrer, 2007). Consequently, it could be hypothesized here that the increase in atomic order with increasing sulphation degrees, namely degrees of  $\text{CaSO}_4$  crystallization, determines a reduction of the fraction of lattice vacancies, which in turn reduces the ions mobility and ultimately the product diffusivity. Altogether, this discussion would reinforce the need of taking into consideration a fractal expression for the diffusivity in the product layer, as proposed in Eq. (4) and verified through the statistical regressions shown in Fig. 2.

Moreover, Eq. (4)

$$D_p = D'_p \theta^{-h} \quad (4)$$

gives a general correlation between the ratio  $D_p/D'_p$  and the dimensionless time  $\theta$  (Eq. (1-d)) not dependent from parameters affecting the sulphation kinetics. In this scenario, the  $D_p/D'_p$  vs.  $\theta$  plot reported in Fig. 4, obtained for  $h=0.91$ , has a general meaning and could be applied, for example, also to cases for which the value of  $\text{SO}_2$  concentration is different. In Fig. 4 it is observed that, as the dimensionless time  $\theta$  increases, the ratio  $D_p/D'_p$  monotonically decreases assuming in particular the value 1 when  $\theta=1$  (i.e., under the present operating conditions, when the actual reaction time values ca. 40 min, that is the characteristic reaction time  $t^*$ ).

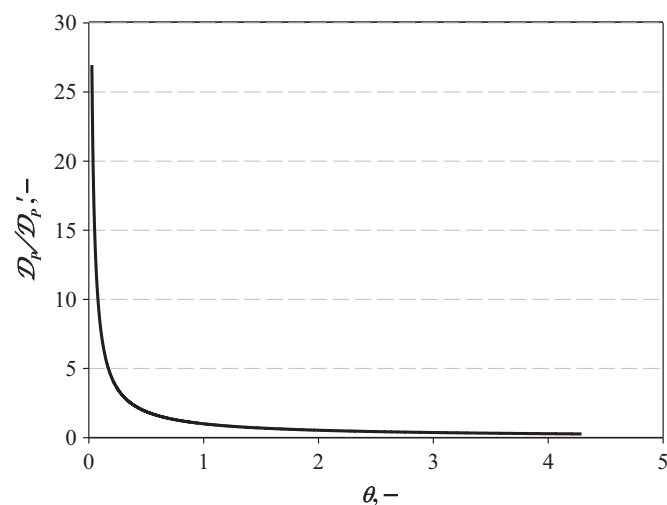


Fig. 4.  $D_p/D'_p$  vs.  $\theta$  pattern according to Eq. (4) with  $h=0.91$ .

## 6. Conclusions

In the present study, concepts borrowed from the fractal theory have been applied to analyze sulphation processes, by invoking the proven development of structural reorganization and crystallographic order. The outcome of this analysis is that diffusivity in the product layer is dependent on time, when the random pore model is used to describe the process with intrinsic sulphation kinetics and diffusion through the  $\text{CaSO}_4$  shell being rate-governing processes. The modeling results of dynamic sulphation tests, performed with limestone in a fluidized bed, showed that a very accurate fitting of the experimental trend could be achieved with the fractal-like rate expression of the random pore model when compared to its classic counterpart. This was particularly so in the first stage of the process. A comparison between diffusivities in pores and in the product layer confirmed that the latter is the rate limiting step for  $\text{SO}_2$  capture, the reported values of diffusivity being 5–6 orders of magnitude smaller. The fractal nature in the time domain of the diffusion process in the  $\text{CaSO}_4$  layer was unraveled by linking product diffusivity to a parameter of structural order, expressing the development of crystallographic order in the product layer. As the value of the parameter of structural order increases with time, crystallization brings about greater atomic order with associated decrease of the lattice defects and reduced ions motion via transport mechanism of vacancies. The fractal scaling equation of diffusivity in the  $\text{CaSO}_4$  shell is consistent with a  $n$ -th order kinetic equation for the rate of change of the parameter of structural order.

Future research efforts should be devoted to the analysis of the microstructural properties of the sorbent as a function of the desulphurization time, for example by means of X-ray diffraction on samples collected at different reaction times. This would enable deeper understanding of the relationships between degree of  $\text{CaSO}_4$  crystallization and fractal exponent of product diffusivity.

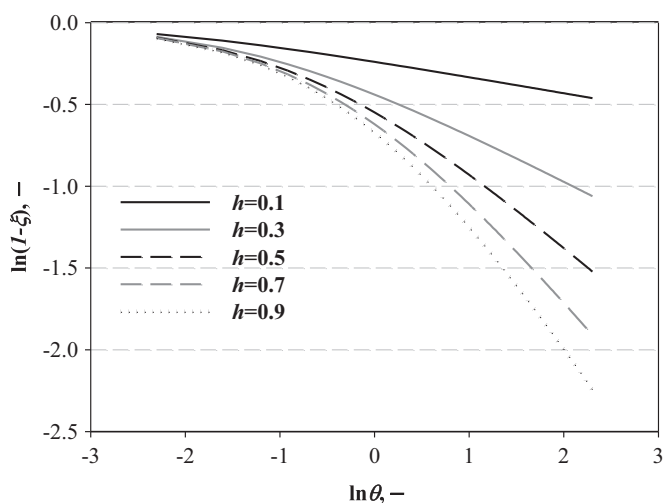
## Appendix A. Derivation of an expression for the parameter of structural order $\xi$

Eq. (3) may be integrated

$$\int_0^\xi \frac{1}{(1-\xi)^n} d\xi = \frac{1}{t^*} \int_0^t dt \quad (\text{A-1})$$

borrowing a procedure developed by Salatino et al. (1999) to model the development of graphitic order of carbon upon thermal





**Fig. A-1.** Relationship between the structural order parameter  $\xi$  and the dimensionless time  $\theta$ , parametric in the fractal exponent  $h$  (Eq. (A-4)).

annealing. Integration of Eq. (A-1) yields, under the assumption of a reaction order  $n \geq 2$  as discussed in the main text (see paragraph following Eq. (4)):

$$\frac{1}{n-1} \left[ \frac{1}{(1-\xi)^{n-1}} - 1 \right] = \theta \quad (\text{A-2})$$

hence

$$\frac{1}{(1-\xi)^{n-1}} = 1 + (n-1)\theta \quad (\text{A-3})$$

or, equivalently

$$1-\xi = \left( 1 + \frac{1}{h}\theta \right)^{-h} \quad (\text{A-4})$$

where

$$h = \frac{1}{n-1} \quad (\text{A-5})$$

with  $h$  generally comprised between 0 and 1 as discussed in the main text. Eq. (A-4) can be regarded as a law of proportionality between  $1-\xi$  and  $\theta^{-h}$ . This can be seen in Fig. A-1, where  $\ln(1-\xi)$  as obtained from Eq. (A-4) is plotted against  $\ln\theta$  for  $\theta \in [0.1; 10]$  and different  $h$ -values: practically straight lines, in particular when  $\theta > 1$ , confirm the hypothesis. It is recalled here that conditions leading to  $\theta > 1$  ( $t > t^*$ ) are relevant to processes characterized by relatively short values of  $t^*$ , which is the case when the diffusion in the product layer overtakes intrinsic reaction kinetics as the rate-limiting step.

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