A COMPARATIVE STUDY OF SO$_2$ SORPTION BY LIMESTONE IN THERMOGRAVIMETRY AND FLUIDIZED BED COAL COMBUSTION

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Abstract. *This work considers the application of thermogravimetry measured to investigate the reaction rate control of SO$_2$ sorption by limestone in fluidized bed coal combustion. A Brazilian dolomite was applied in both thermogravimetry and a bubbling fluidized bed combustor burning a Brazilian CE4500 coal. The limestone was applied in particle sizes of 385, 545, 725 and 775 μm, and a coal particle size of 383 μm was apllied in the fluidized bed experiments. The thermogravimetric experiments were carried out in conditions as close as possible to those observed in the fluidized bed combustion process. Intrinsic reaction rate coefficients were determined through thermogravimetry in atmospheres containing 65% of synthetic air, 15% of CO$_2$ and 20% of SO$_2$, at four different temperatures (between 800 and 890 ºC). Global reaction rate coefficients were obtained from the fluidized bed combustor experiments. Temperatures between 798.2 and 886.6 ºC, U/U$_{mf}$ between 5.6 and 10.8 m/s, and (Ca+Mg)/S molar feeding ratios between 3.7 and 11.9 kmol(SO$_2$)/kmol(Ca+Mg) were applied. The rate coefficients of the fluidized bed global reaction were composed with the thermogravimetric intrinsic reaction rate coefficients in an attempt to establish the effects of mass transfer on sulfur absorption in the fluidized bed combustor. The calculations provided unrealistic results showing that the thermogravimetric conditions that were applied were not realistic enough. It was concluded that more realistic thermogravimetric conditions are required so that the composition of intrinsic and global reaction rate coefficients can allow for the analyses of reaction rate control in fluidized bed reactors.*

Keywords: Dessulfurization, coal, limestone, thermogravimetry, combustion, fluidized bed.

1. INTRODUCTION

In fluidized bed coal combustion limestone is usually injected directly into the combustion chamber, promoting an "in locus" sulfur removal in the same place in which sulfur oxides are formed (Van Hout and Delmon, 1979). The sorption of sulfur oxides by calcium depends largely on complex flow patterns that develop in the fluidized bed combustor. The reaction rates are controlled by chemical kinetics and mass transport effects of reactive gases.

The global reaction of desulfurization by calcined limestone can be represented by $CaO + SO_2 + {}^1\!/_2O_2 \rightarrow CaSO_4$. According to Moss (1975), sulfation can occur through two different routes: [1] $CaO + SO_2 \rightarrow CaSO_3$ and $CaSO_3 + {}^1\!/_2O_2 \rightarrow CaSO_4$; or [2] $SO_2 + {}^1\!/_2O_2 \rightarrow SO_3$ and $CaO + SO_3 \rightarrow CaSO_4$. At temperatures below 865 ºC, the first two reactions [1] predominate. Above 865 ºC all the reactions, [1] and [2], develop significantly. The kinetics of chemical reactions controls reactions for low temperatures. At higher temperatures, the diffusion in the particles phase assumes the control of the reaction. At some point, the resistance to diffusion through the layer of the reagent becomes the controlling factor of the reaction.

The mechanisms that actually control the sulfation and the effects of concentrations of O$_2$, SO$_2$, SO$_3$ and H$_2$O on the process are questions that remain open (Dennis and Hayhurst, 1990, Hu et. Al., 2006). Experimentation has shown that the concentration of O$_2$, and not SO$_3$, is the one that really limits the reaction extent of sulfation. Even when there is the formation of an outer layer of CaSO4, the initial sulfation rate occurs the same way by SO$_2$ or SO$_3$ and O$_2$, and is not affected by the concentration of O$_2$ in the air fed in the process. Therefore, the sulfation by SO$_2$ occurs in function of the formation of intermediate CaSO$_3$. After the outer layer of CaSO$_4$ is formed, the O$_2$ concentration will affect the sulfation of CaO by SO$_2$. The sorption of sulfur dioxide decreases with the increase in the O$_2$ concentration. Apparently the concentration of O$_2$ affects the size of the crystalline structure or the number of cracks in the layer of CaSO$_4$ produced, thus affecting the diffusion rate through the layer formed. The effective coefficient of the reaction rate decreases with the conversion degree and with an increase in the concentration of O$_2$ (Dennis and Hayhurst, 1990).

The literature has shown a considerable variety of mathematical models for desulfuration from limestones (Székely and Evans, 1970, Székely and Evans, 1971, Hartman and Coughlin, 1976, Ramachandran and Snith, 1977, Dennis and Hayhurst, 1986, Schouten and Van den Bleek, 1988, Daniell et al., 1988, Dennis and Hayhurst, 1988, and Lyngfelt Lackner, 1989, Dam-Johansen et al., 1991, Lin et al., 1991). These models differ basically in the assumptions formulated for the mechanisms controlling the reaction. The reaction resistances are due to the mass transport in the region outside the particle, gases diffusion within the macro and micropores, gases diffusion through the layers reacted inside the pores, and the kinetics of chemical reactions at the solid product/reagent interface. In general, combinations of these resistances are taken into account. The reaction models most commonly assumed are *unreacted-core* or *shrinking partially reacted-core* (Székely and Evans, 1970, Dam-Johansen et al., 1991, Dam-Johansen and Ostergaard,

1991), in combination with descriptive models of porosity of *grain-micrograin* (Székely and Evans, 1970, Schouten and Van den Bleek, 1988, Dam-Johansen et al., 1991), and *single pore* (Székely and Evans, 1970, Ramachandran and Snith, 1977, Dennis and Hayhurst, 1986).

Several researches reported in the literature are related to studies of SO_2 sorption by limestone in thermogravimetric systems. Zarkanitis and Sotirchos (1989) showed that the evaluation of limestone for SO_2 sorption should not be based only on porosity and pore surface area, but also on the sizes distribution and interconnections structure. Wiedemann et al. (1990) showed that the sulfation rate of limestones previously calcined depends on atmosphere, temperature and particles size. Fuertes et al. (1994) showed that the direct sulfation of limestone under high CO_2 concentrations develops according to the *unreacted core* model. They concluded that the final control of the reactive process was due to the ionic diffusion in the solid state through the layers reacted. Fuertes and Fernandez (1995) studied the kinetics of calcium sulfate decomposition and observed a strong influence of temperature and O_2/SO_2 concentrations on the process. They concluded that the decomposition is controlled by chemical kinetics.

The literature on sorption of sulfur oxides by limestones, including researches conducted in the NETeF (Milioli, 1996, Milioli et al., 2004, Pagliuso et al., 2002, Camargo et al., 2003, Silva Filho, 2002, Crnkovic, 2003; Ávila, 2005; Ávila, 2008), shows that the evolution of porosity during calcination and sulfation of limestones is the major determining factor for its final reactivity, considering the typical residence time in the fluidized bed reactors. Under typical conditions, a limestone particle remains highly reactive for no longer than 2 or 3 minutes, while common residence times take hours. Whatever its residence time, each limestone particle probably reaches its maximum reactivity in the reactor, which occurs when the pores structure is virtually blocked or inaccessible.

Due to the great heterogeneity and structural complexity of limestone, it is virtually impossible to build accurate reactive models based on the knowledge of the evolution of the particles' physical structure in both calcination and sulfation reactions. This development is highly transient, specific for each type of limestone, and even different for each size and shape of individual particles. The current state of the art makes it clear that there is no way to formulate accurate generic physical models to calcinations and sulfation; it is more practical to treat all the intrinsic phenomena closely related to the properties and characteristics of the limestone in block. Actually they cannot be easily discerned. Furthermore, intrinsic effects can be clearly discerned to external effects imposed by the mass transport in the fluidized bed.

This paper deals with the determination of sorption rate coefficients of SO_2 by limestone in the combustion in atmospheric fluidized bubbling of coal. Intrinsic factors are determined by thermogravimetry and global reaction rate coefficients are determined in the fluidized bed reactor. The global sulfation rate coefficients obtained in the fluidized bed were compared to the intrinsic reaction rate coefficients obtained through thermogravimetry.

2. EXPERIMENTAL

The experimental systems utilized in this study were a thermogravimetric analyzer (TGA) and a bench-scale fluidized bed combustor (Fig. 1).
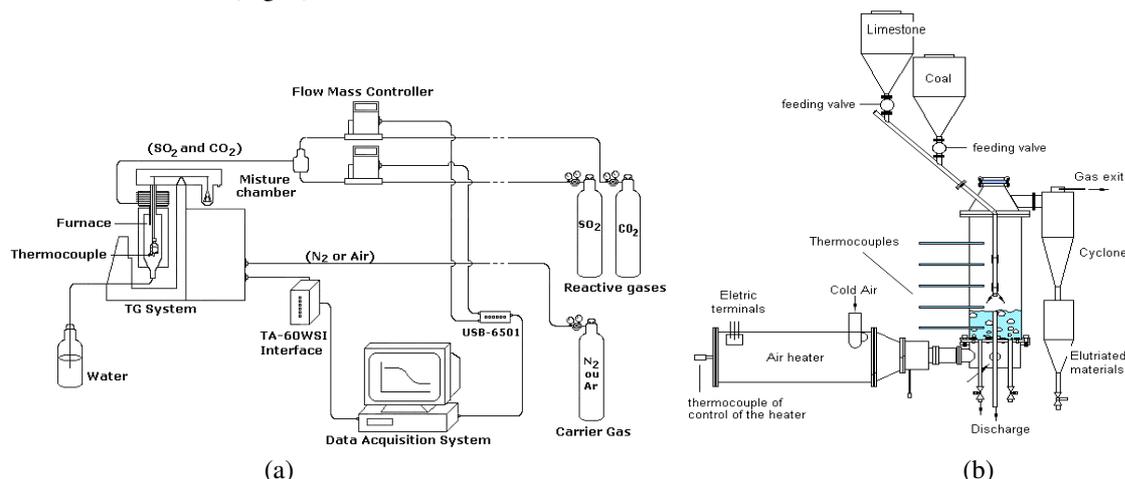
Figure 1. Experimental systems: (a) Sketch system TG (SHIMADZU – TGA-51) and (b) Sketch of the bench scale fluidized bed plant used in the experiments.

Figure 1(a) presents a sketch of TGA, data acquisition system and trajectory of the gas until the TGA furnace. Only the carrier gas (N_2 or Air), which is controlled by an internal flowmeter, flows through the balance mechanism. When the use of reactive gases (CO_2 and SO_2) is required, these gases do not come into contact with the balance mechanism, and are injected directly into the furnace by a mass flow control (Aalborg). The control of the mass flow of the gas reagents is accomplished by the programmed system control USB-6501 and *Lab View*, both from *National Instruments Corp.*

Figure 1(b) shows a sketch of the bench scale fluidized bed plant used in the experiments. The reactor is an atmospheric bubbling fluidized bed with 160 mm of internal diameter.

Previously to the start of the reactor, it is necessary to prepare the experimental system taking into account the following aspects: cleanliness and assembly of the system, preparation of solids (coal, limestones and sand) and calibration (gas analyzers, thermocouples and system of feeding of solids). Two rotating valves are employed for the feeding systems of coal and limestone. The feeding rates of coal and limestone in the reactor are given by the curves of calibration of the respective rotating valves, applying different tensions (V) for each solid.

Initially the bed is formed by 3 kg of sand, it fluidizes with heated air until its temperature has reached about 500 ^{o}C and in the fluidizing velocity required. Under these conditions coal is added to the reactor until the temperature has reached approximately 850 ^{o}C. Samples of the combustion gases are continuously extracted from the gas analyzers until the regimen condition has been reached. Under these conditions the limestone is added to the reactor. The gaseous emissions are collected in the discharge of the cyclone, while the consequent variations of the exit concentrations of SO_2, CO_2, and O_2 are continuously measured in Horiba Enda 1400 gas analyzers.

This reactor was designed and built at Group of Thermal and Fluids Engineering (EESC/USP). Paludo et al. (2006) presented this experimental system, including the main details of construction and project of the plant, stages of tests performed, problems and solutions obtained.

The following particles materials were used in the experiments: a particular Brazilian southern bituminous coal called EC4500 (e.g., energetic coal with higher calorific value of 4500 kcal kg^{-1}) and a dolomitic limestone from Ipeúna-SP. Table 1 shows their elementary chemical composition.

Table 1. Elementary chemical composition of coal and limestone.

	Composition (% mass/mass)[1]					**Proximate Analysis [2]**		
Coal	S	C	N	H	Moisture	Volatile matter	Fixed Carbon	Residual Ash
	2.35	49.38	1.06	3.66	1.2	24.5	23.1	51.2
	Composition (% mass/mass)[3]							
Dolomite	Ca	Mg	Fe	Al	Sr	K	Mn	
	17.07	11.73	0.32	0.42	0.08	0.13	0.09	

[1] *Costa (2005);* [2] *Ávila et al. (2007);* [3] *Crnkovic (2003)*

Dolomite samples weighing 10.0±0.5 mg were used in all thermogravimetric experiments. These small samples allowed minimizing the inter-particle mass transfer resistances by spreading the particles in a monolayer at the bottom of the crucible (alumina, 6 $\varnothing \times$ 2.5 mm). The dolomite was used in four different average sizes: 385, 545, 775 µm (between the mesh apertures of two consecutive ASTM laboratory sieves) and 725 µm (composition of two average sizes: 650 and 775 µm). Previously to sulfation, the sample was calcined inside the analyzer in 100% of air atmosphere, applying a heating rate of 50 ^{o}C min^{-1} until 550 ^{o}C; then this heating rate was changed to 10 ^{o}C min^{-1} until a desired temperature had been reached and the decomposition had been complete. Next 15 % of CO_2 and 20% of SO_2 were added to the atmosphere, and the isothermal sulfation developed. This condition was kept for 30 min. Four different sulfation temperatures were applied (between 800 and 890 ^{o}C). All experiments were performed in three replicates and the averaged results were produced. From the measurements, the intrinsic coefficient of reaction rate was determined for the limestone sulfation.

In fluidized bed reactors, the tests were conducted with continuous feeding of coal and dolomite. The exit concentrations of combustion gases as well as entrance concentrations of fluidizing gases were measured. Among these gases are SO_2, O_2 and CO_2. In air excess, fluidization velocity (U/U_{mf}), particle size and process temperature were established having in view typical operation conditions. The varied parameters for analysis were fluidization velocity (U/U_{mf} between 6 and 11), temperature (between 800 and 900 ^{o}C), particle mean size of limestone (385, 545, 724 and 775 µm) and (Ca+Mg)/S (between 6 and 12 $\text{kmol}_{(Ca+Mg)} / \text{kmol}_{SO_2}$). From the measurements, the global reaction rate coefficient was determined for the limestone sulfation.

3. DATA REDUCTION METHODOLOGY

3.1. Intrinsic Coefficient of Reaction Rate

In thermogravimetric experiments, the temporal changes in the sample's masses of limestone are measured during sulfation. From these measurements, the intrinsic coefficient of reaction rate is determined.

The possibility of controlling the reaction rate by intrinsic factors, external or combined, is considered. Correlations may be established for the reaction rate by taking into account each of these conditions. The global reactions of calcination and sulfation can be represented by the following equations:

$$1 \text{ CaMg(CO}_3)_2 \rightarrow 1 \text{ CaO} + 1 \text{ MgO} + 2\text{CO}_2 \tag{1}$$

$$1 \text{ CaO (s)} + 1 \text{ SO}_2 \text{ (g)} + \tfrac{1}{2}\text{O}_2 \rightarrow 1 \text{ CaSO}_4 \text{ (s)} \tag{2}$$

$$1 \text{ MgO (s)} + 1\text{SO}_2 \text{ (g)} + \tfrac{1}{2}\text{O}_2 \rightarrow 1 \text{ MgSO}_4 \text{ (s)} \tag{3}$$

For the intrinsic reaction control as a composition of intra-diffusion and chemical kinetics effects, are assumed that the consumption rate of SO_2 by a calcium particle ($\Re_{SO_2}$), given by

$$\Re_{SO_2} = \left(4\pi r^2\right) m k_S C_{SO_2,r}^1 C_{O_2,r}^{0,5} \tag{4}$$

where k_S is the coefficient of effective intrinsic reaction rate, m is the mass of the solid reactive fraction of particles (Ca+Mg), $C_{O_2,r}$ and $C_{SO_2,r}$ are O_2 and SO_2 concentrations, respectively, on the external surface of the particle.

Assuming the O_2 concentration has no significant effect on the reaction rate and only the SO_2 concentration and the mass of (Ca+Mg) limit the rate of sorption, one has

$$\Re_{SO_2} = \left(4\pi r^2\right) m k_S C_{SO_2,\infty} \tag{5}$$

Note that under differential conditions in TG experiment, $C_{SO_2,r} \approx C_{SO_2,\infty}$.

The rate of total weight gain of limestone sample in the sulfation process is given by

$$\frac{dm_A}{dt} = n_A \cdot \Re_{SO_2} \cdot \left(W_{SO_2} + \tfrac{1}{2}W_{O_2}\right) , \; where, \; n_A = \frac{m_A}{\tfrac{3}{4}\pi r^3 \rho_A} \tag{6}$$

where m_A is the sample weight, W stands for the molecular mass of the concerning species, n_A is the number of particles in the sample (assuming spherical particles of radius r) and ρ_A is the density of the limestone.

Substituting Eq. (4) into Eq. (6), one has

$$m k_S = \frac{r\rho_A}{3m_{A0}\left(W_{SO_2} + \tfrac{1}{2}W_{O_2}\right) C_{SO_2,\infty}}\left(\frac{dm_A}{dt}\right) \tag{7}$$

The integration of Eq. (7) in time, considering a residence time τ, gives an average effective intrinsic coefficient of SO_2 sorption rate by limestone ($\overline{m k_S}$):

$$\overline{m k_S} = \frac{1}{\tau}\int_0^\tau \left(m k_S\right)dt = \frac{r\rho_A}{3m_{A0}\left(W_{SO_2} + \tfrac{1}{2}W_{O_2}\right) C_{SO_2,\infty}} \cdot \frac{1}{\tau}\int_0^\tau \left(\frac{dm_A}{dt}\right)dt \tag{8}$$

3.2. Global Reaction Rate Coefficients

In fluidized bed reactors, as the flow around the reaction particles occurs at a low Reynolds number, the external mass transportation is diffusive (Avedesian and Davidson, 1973). To establish the reactions rate under external control, Fick's diffusion law is applied to describe the gases transportation in the fluidized medium (O_2 transportation toward an individual particle of coal, and SO_2 transportation toward an individual particle of limestone). For the combustion, the reaction rate under external control will be equal to the consumption rate of O_2 and for the sulfation, the reaction rate under external control will be equal to the consumption rate of SO_2 on the external surface of limestone particles ($C_{SO_2,r}$). Assuming constant the SO_2 concentration in the gas far from the particle surface, the problem solution about SO_2 diffusion around a particle of radius r is

$$\Re_{SO_2} = 4\pi E r \left(C_{SO_2,\infty} - C_{SO_2,r}\right) \tag{9}$$

In Eq. (9) E represents the effective diffusion coefficient of SO_2 in fluidized environment, considering the presence of the particulates. The Sherwood number (Sh) is can defined as

$$Sh = \frac{2E}{D_G}. \tag{10}$$

where E is related to the molecular diffusion coefficient of gas-gas (D_G). Then,

$$\Re_{SO_2} = 2\pi Sh D_G r \left(C_{SO_2,\infty} - C_{SO_2,r}\right) \tag{11}$$

It is considering the more general case of intrinsic/external controlling rate of reaction combined, the Eqs. (5) and (11) must be satisfied simultaneously. The SO_2 concentration on the surface of the particle ($C_{SO_2,r}$), which is unknown, is eliminated in equations, one has:

$$\Re_{SO_2} = \left(\frac{1}{\dfrac{2r}{Sh D_G} + \dfrac{1}{m k_S}}\right) 4\pi r^2 C_{SO_2,\infty} \tag{12}$$

A global rate coefficient of reaction (K_S) is defined:

$$\frac{1}{K_s} = \frac{2r}{ShD_G} + \frac{1}{mk_s} \tag{13}$$

The terms on the right of Eq. (13) represent, respectively, the resistances to external and intrinsic reaction.

The sorption rate of SO_2 by a calcium particle ($\Re_{SO_2}$) results in

$$\Re_{SO_2} = \left(4\pi r^2\right) K_s C_{SO_2,\infty} \tag{14}$$

The sorption rate of SO_2 for all the limestone particles in the bed (R_{SO_2}) is given by

$$R_{SO_2} = UA\left(C_{SO_2}^C - C_{SO_2}^A\right) = n_A \cdot \Re_{SO_2} \, , \, where \, , \, n_A = \frac{M_A}{\frac{3}{4}\pi r^3 \rho_A} \tag{15}$$

where U is the superficial velocity of fluidization, A is the area of cross section of the fluidized bed, n_A is the total number of limestone particles in the bed and M_A is the mass of limestone in the fluidized bed reactor under continuous operation.

It is assumed an average representative K_s for all limestone particles in the bed, one has

$$K_s = \frac{\rho_A r}{3M_A} UA \frac{\left(C_{SO_2}^C - C_{SO_2}^A\right)}{C_{SO_2,\infty}} \tag{16}$$

The fluidized bed is considered to be well mixed, and the entire sorption occurring in the bed, $C_{SO_2,\infty} \to C_{SO_2}^A$, one has

$$K_s = \frac{\rho_A r}{3M_A} UA \frac{\left(C_{SO_2}^C - C_{SO_2}^A\right)}{C_{SO_2}^A} \tag{17}$$

3.3. Correlation Between the Coefficients of Intrinsic Reaction Rate and Averege Effective Intrinsic Reaction Rate

The variation rate of transient mass of the reactive material (dm/dt) can be given by

$$-\frac{dm}{dt} \propto m^a C_{SO_2}^b C_{O_2}^c \quad ou \quad -\frac{dm}{dt} \propto m^a C_{SO_3}^d \tag{18}$$

where m is the mass transient of the reactive material (Ca+Mg) available for the reaction, $C_{SO_2}^b$, $C_{O_2}^c$ and $C_{SO_3}^d$ are the concentrations of reactive gases in the atmosphere and (a, b, c, d) represents the orders of the global reaction to the mass and each of the reagent gases.

A first-order reaction is considered regarding the mass of the sample (a=1), and the reaction is assumed to be independent of the concentration of reaction gases (b=c=d=0). Therefore, the reaction is assumed to be of order zero regarding the concentrations of reacting gases (differential conditions are applied). Under those assumptions, the reaction rate becomes:

$$-\frac{dm}{dt} \propto m \tag{19}$$

Introducing a reaction rate coefficient (*k*) in the Eq. (19), one has:

$$-\frac{dm}{dt} = k\,m \tag{20}$$

k is different from k_s, since the latter occurs in the reaction affected by the gaseous reactants´ concentrations.

The relation between coefficients k_s and k is given by Eqs. (7) and (20):

$$\overline{mk_s} = \frac{r\rho_A\left(Y_{Ca} + Y_{Mg}\right)}{3m_{A0}\left(W_{Ca}Y_{Ca} + W_{Mg}Y_{Mg}\right)C_{SO_2,\infty}} \cdot \frac{1}{\tau}\int_0^\tau k\,m\,dt \tag{21}$$

where Y is the molar fractions of Ca and Mg.

4. RESULTS AND DISCUSSION

A total of 19 tests of coal combustion and desulphurization by limestone were performed in the bench scale fluidized bed. Figure 2(a) shows the transient concentration profiles of CO_2, O_2 and SO_2 obtained during the process of desulfurization by limestone in the combustion of coal. It is possible observe that initially there are high concentrations of SO_2 and after adding limestone into the reactor the concentration decrease.

Thermogravimetric tests with conditions as close as possible to those of temperature and particle size conducted in fluidized bed were carried out. Figure 2(b) shows the result of the sulfation experiments for dolomite of 725 µm at 900°C in TGA. The TG curve shows both, calcination and sulfation events, as well as DTG and temperature profiles.

The sets of curves for all the other experiments in fluidized bed combustion (FBC) and thermogravimetric (TG) conditions were similar to those showed in Figs. 2(a) and (b), respectively.
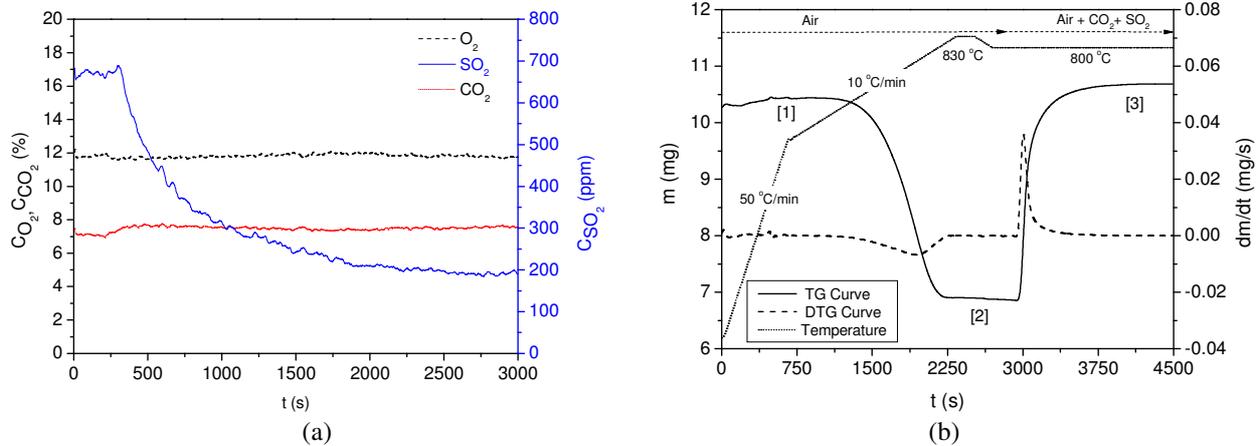
Figure 2: (a) Exit transient concentration profiles of O_2 (C_{O_2}), CO_2 (C_{CO_2}) and SO_2 (C_{SO_2}) in function of time (limestone particle size = 725 µm; T = 833 °C; U/U_{mf} = 6,6; (Ca+Mg)/S = 6,3); (b) Profiles of calcinations followed by sulfation at 800 °C, for the dolomite of 725 µm, in atmosphere of 65%Air+15% CO_2+20%SO_2.

From the tests obtained, in principle it would be possible to analyze the reaction control of the limestone sulfation in fluidized bed reactor for coal combustion. Therefore, the thermogravimetric results, Eq. (8), would be combined with results obtained in the fluidized bed reactor, Eq. (17), and then they would determine the diffusive resistance to sulfation.

The analysis of reaction control would be performed from the values of resistance to the global reaction $(1/K_s)$, kinetic $(1/mk_s)$ and diffusive $(2r/ShD_G)$ in function of the variation of the process parameters (particles size, temperature, fluidization velocity and ratio (Ca+Mg)/S). From the diffusive resistance, the number of Sherwood (Sh), which relates the diffusion coefficient of effective mass in the process with the molecular diffusion coefficient of gas-gas, could also be obtained.

For this proposal, thermogravimetric tests were performed under conditions which are as similar as possible to those applied in the fluidized bed reactor (the same size and process temperatures). However, as there occurs a direct sulfation process (calcination and sulfation simultaneous) under the fluidized bed conditions, it could not be possible to obtain direct sulfation rates due to the experimental limitation in the thermogravimetric tests. It was also observed that even if it were possible to separate the variations in mass due to the calcination and sulfation, the sulfation results obtained in thermogravimetric analyzer would be too low and variable temperatures would not be similar to the conditions applied in the fluidized bed.

Therefore, calcination tests were performed followed by sulfation under isothermal condition. In the sulfation process, 15% CO_2 were added to the atmosphere to be approximate to those observed in fluidized bed conditions. Differential conditions were imposed by applying high concentrations of the reactant gases to the atmosphere (20%), so that transport effects external to the particles were eliminated and the reaction results could be controlled by intrinsic or intra-particle kinetics and diffusion mechanisms.

Table 2 shows the results obtained for K_S (fluidized bed conditions) and $\overline{mk_S}$ (thermogravimetric conditions) and Fig. 3 shows the same results in function of temperature.

It is observed in Tab. 2 and Fig. 3 that $\overline{mk_S}$ values resulted two orders of magnitude lower those obtained to K_S.

The Sherwood number (Sh) is given by:

$$\frac{2r}{ShD_G} = \frac{1}{K_s} - \frac{1}{\overline{mk_s}} \quad or \quad Sh = \frac{2r}{D_G} \cdot \frac{\overline{mk_s} \cdot K_s}{\overline{mk_s} - K_s} \tag{22}$$

It is observed that Sh (Eq. 22) is extremely sensitive in relation to K_s and $\overline{mk_s}$ values. For instance, when the particle size is 725 µm and T = 1103.15 K, the behavior shown in Fig. 4 is obtained. Depending on the values of K_s and $\overline{mk_s}$, positive or negative values may be obtained for Sh, $\overline{mk_s}$, but only positive values are realistic.

In this work the diffusive resistance $(2r/ShD_G)$ was negative, as $K_s > \overline{mk_s}$. Obviously, this result is impossible. In this case, it was not possible to compose intrinsic coefficients ($\overline{mk_s}$) obtained under thermogravimetric conditions with global coefficients of reaction (K_s) obtained in fluidized bed conditions to determine the Sherwood number.

Negative values for the Sherwood numbers indicate incompatibility between the experimental measurements obtained under thermogravimetric and fluidized bed conditions.

In fact, it was concluded that the coefficients obtained in the thermogravimetric analyzer do not apply to the process in fluidized bed reactor, as the additional resistances to reaction in the bed, due to mass transport, could only reduce the coefficient of reaction rate and never increase it.

Table 2: Comparison between the results obtained in fluidized bed combustor and those in thermogravimetry is analyzer.

d_A (mm)	T (°C)	FLUIDIZED BED						THERMOGRAVIMETRIC		
		H_{Leito} (mm)	U/U_{mf}	$\dfrac{(Ca+Mg)}{C_{SO_2}^A}$	M_A (kg)	$\dfrac{(C_{SO_2}^C - C_{SO_2}^A)}{C_{SO_2}^A}$	K_S (m/s)	C_{SO2} (kmol/m^3)	m_{A0} (kg)	$\overline{mk_s}$ (m/s)
0.385	846.05	120	7.6	11.9	0.446	1.55	2.59E-02	2.03E-03	1.00E-05	3.39E-04
0.545	850.35	120	7.5	11.9	0.446	1.20	9.29E-03	2.03E-03	1.03E-05	4.33E-04
0.545	870.31	120	10.1	6.5	0.324	1.41	1.93E-02	1.98E-03	1.01E-05	6.50E-04
0.545	886.56	120	7.5	8.4	0.381	1.05	1.71E-02	1.93E-03	1.01E-05	5.19E-04
0.725	798.2	120	10.2	6.0	0.298	3.81	3.23E-02	2.09E-03	1.01E-05	8.31E-04
0.725	799.74	120	6.6	6.2	0.316	0.98	1.98E-02	2.09E-03	9.86E-06	5.66E-04
0.725	800.16	120	8.6	6.1	0.312	1.03	3.14E-02	2.09E-03	9.86E-06	6.99E-04
0.725	801.73	180	6.0	6.2	0.425	1.46	4.33E-02	2.09E-03	9.86E-06	4.21E-04
0.725	817.81	180	8.0	6.1	0.419	1.22	3.62E-02	2.03E-03	1.03E-05	4.84E-04
0.725	832.83	120	6.5	6.2	0.316	1.12	4.45E-02	2.03E-03	1.01E-05	6.05E-04
0.725	836.22	120	10.8	6.1	0.299	1.34	5.29E-02	2.03E-03	1.01E-05	1.06E-03
0.725	846.39	120	7.2	6.2	0.306	3.22	2.31E-02	1.98E-03	1.01E-05	5.58E-04
0.725	848.82	180	8.4	6.1	0.419	2.02	2.15E-02	1.98E-03	1.01E-05	4.96E-04
0.725	851.01	180	6.4	6.2	0.425	2.61	7.18E-02	1.98E-03	1.01E-05	4.01E-04
0.775	807.45	120	9.3	6.1	0.311	1.95	3.19E-02	2.09E-03	1.03E-05	7.67E-04
0.775	811.82	120	6.6	6.5	0.325	1.30	2.47E-02	2.09E-03	1.03E-05	6.61E-04
0.775	842.73	120	7.5	8.1	0.361	1.17	2.93E-02	2.03E-03	1.00E-05	5.43E-04
0.775	851.1	120	9.7	6.0	0.309	5.23	2.37E-02	1.98E-03	9.74E-06	7.92E-04
0.775	851.56	120	7.2	6.4	0.32	1.19	1.68E-02	1.98E-03	9.74E-06	6.59E-04
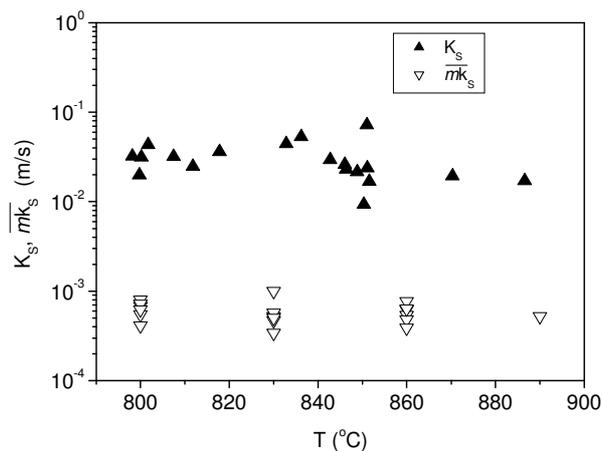
Figure 3: Magnitude Order of the average results obtained in thermogravimetric ($\overline{mk_s}$) and fluidized bed (K_S) in function of temperature.
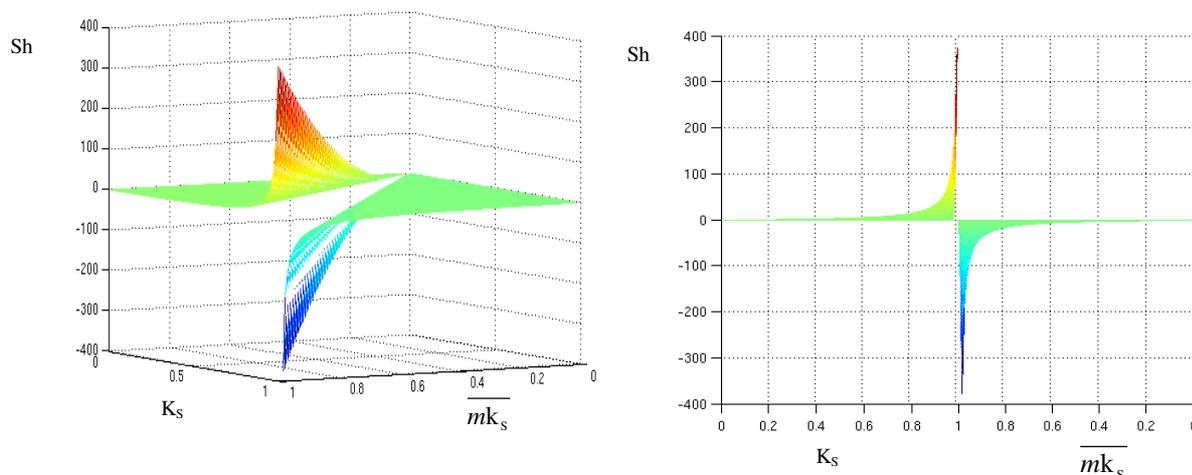
Figure 4: Behavior of Sh in function of the parameters $\overline{mk_s}$ and K_S.

An atmosphere with 20% of SO_2 (200000 ppm) was applied to thermogravimetric experiments to ensure differential conditions, so that mass transport could be eliminated. In steady state, the SO_2 concentrations in fluidized bed reactor after feeding limestone to the bed ($C_{so_2}^A$) ranged between 418 and 116 ppm and the global coefficients of average sulfation rate were inversely proportional to the SO_2 concentration (Fig.5).
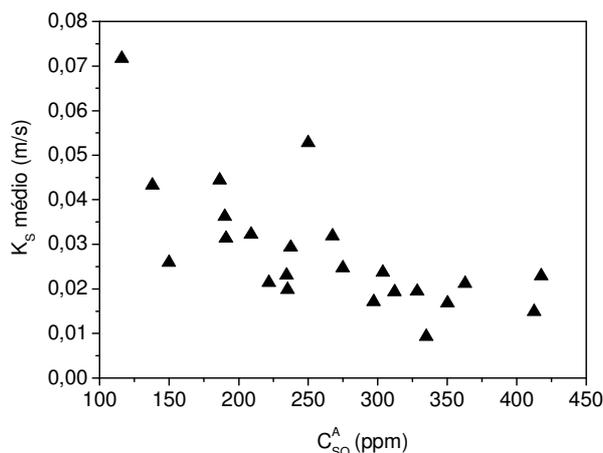
Figure 5: Global coefficient of rate reaction (K_S) in function of SO_2 concentration ($C_{so_2}^A$) after adding limestone to the bed.

These results show that if there were high SO_2 concentrations in the fluidized bed like those applied in thermogravimetry, the global coefficients of sulfation rate would be lower than the ones observed. Therefore, the intrinsic factors currently measured in thermogravimetric tests would be relevant to the fluidized bed process.

However, it is not realistic to apply 20% SO_2 to the fluidized bed reactor. It should be sought intrinsic coefficients under thermogravimetric conditions with similar concentrations of SO_2 those practiced fluidized bed reactor, i.e., between 418 and 116 ppm.

5. CONCLUSIONS

The global reaction rate coefficients were composed of the thermogravimetric intrinsic reaction rate coefficients, in an attempt to establish the effects of mass transfer on sulfur absorption in the fluidized bed combustor. The calculations provided unrealistic results showing that the thermogravimetric conditions that were applied were not realistic enough. It was concluded, that more realistic thermogravimetric conditions are required so that the composition of intrinsic and global reaction rate coefficients can allow for the analyses of reaction rate control in fluidized bed reactors.

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7. REFERENCES

Avedesian, M. M.; Davidson, J. F. (1973), Combustion of carbon particles in a fluidised bed, Trans. Inst. Chem. Engrs., 51, p.121-131.

Ávila, I. (2005). Estudo termogravimétrico da absorção de dióxido de enxofre por calcário, 97p. Dissertação (Mestrado), Universidade de São Paulo, Escola de Engenharia de São Carlos, São Carlos, 2003.

Ávila, I. (2008), Um Estudo da Sorção de SO_2 por Calcário em Analisador Termogravimétrico e na Combustão de Carvão em Leito Fluidizado. 2008, 10f. Tese (Doutorado) - Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2008.

Ávila, I.; Crnkovic, P.M. ; Milioli, F.E. (2007), Caracterização da combustão de um carvão mineral energético Brasileiro. 8º Congreso Iberoamericano de Ingenieria Mecánica – CIBIM 8, 22 a 25 de Outubro de 2007, Cusco – Peru (publicado em CD-ROM).

Camargo, F. L. ; Pagliuso, J. D. ; Milioli, F. E. (2003). Conversion and global reaction rate coefficient in the absorption of SO_2 by different types of limestone in a fluidized bed reactor. Engenharia Térmica, v. 3, p. 50-57,

Costa, M.C.D. (2005), Emissões poluentes na combustão em leitos fluidizados de carvão mineral, 114p Tese (Doutorado), EESC-USP, São Carlos.

Crnkovic, P. C. G. M. (2003), Análise termogravimétrica para a determinação de fatores que afetam a eficiência de sorção de SO_2 por calcários na combustão de carvões. Tese (Doutorado), IQSC-USP, São Carlos, 127p.

Dam-Johansen, K.; Ostergaard, K. (1991) High-Temperature Reaction between Sulphur dioxide and Limestone: (I) Comparison of limestones in two laboratory reactors and a pilot plant; (II) An improved experimental basis for a mathematical model; (III) A grain-micrograin model and its verification; (IV) A discussion of chemical reaction mechanisms and kinetics. Chemical Engineering Science, Vol.46, No.3, p.827-859.

Daniell, P.; Soltani-Ahmadi, A.; Kono, H.O. (1988), Reaction kinetics of the SO2-CaO system - pore closure model, Powder Technology, 55, p.75-85.

DENNIS, J.F.; HAYHURST, A.N. (1986), A simplified analytical model for the rate of reaction of SO_2 with limestone particles, Chemical Engineering Science, 41, p.25-36.

Dennis, J.F.; Hayhurst, A.N. (1988), A model for the continuous desulphurisation of a fluidised bed combustor using limestones, dolomites or related solid sorbents, Journal of the Institute of Energy, June, p.98-109.

Dennis, S.; Hayhurst, A.N. (1990) Mechanism of the sulphation of calcined limestone particles in combustion gases. Chemical Engineering Science, 45 1175-1187.

Fuertes, A. B.; Velasco, G.; Fuente, E.; Alvarez, T. (1994) Study of the direct sulfation of limestone particles at high CO_2 partial pressures. Fuel Processing Technology, 38, 181-192.

Fuertes, A.B.; Fernandez, M.J. (1995). Kinetics of the calcium sulphate decomposition, Trans. Inst. Chem. Engrs., 73-A, 854-862.

Hartman, M.; Couchlin, R. W. (1976), Reaction of Sulfur Dioxide with limestone and the grain model, AIChE J., v.22, n.3, p.490-498.

Hu, G; Dam-Johansen, K.; Wedel, S.; Hansen, J. P. (2006), Review of the Direct Sulfation Reaction of Limestone, Progress in Energy and Combustion Science, 32, p.386–407.

Lin, W.; Senary, M.K.; Van Den Bleek, C.M. (1991), SO2/NOx emissions in FBC of coal: experimental validation of the DUT SURE-model with data from the Babcock and Wilcox 1-foot x 1-foot AFBC unit, 11th Internatinal Conference on Fluidised Bed Combustion, Vol. 3, ASME, New York, p.649-654.

Lyngfelt, A.; Leckner, B. (1989), Sulphur capture in fluidized bed boilers: the effect of reductive decomposition of CaSO4, The Chemical Engineering Journal, p.4059-69.

Milioli, F. E. (1996), Atmospheric bubbling fluidized bed combustion: application to high ash coals and approach to scientific research. Revista Brasileira de Ciências Mecânicas, Rio de Janeiro, v. XVIII, n. 2, p. 127-142.

Milioli, F.E., Pagliuso, J.D., Crnkovic, P.M., Costa, M.C.D., da Silva, G.F. & Camargo, F.L., Absorption of sulfur dioxide by limestones for particulate sizes and temperatures typical to atmospheric bubbling fluidized bed coal combustion, submitted to Chemical Engineering Science (2004).

Pagliuso, J.D.; Milioli, F.E.; Crnkovic, P.M.; Costa, M.L.D.; Silva, G.F.; Camargo, F.L. (2002) Absorption of sulfur dioxide by different types of limestone in fluidized bed reactor and TGA. AICHE Annual Meeting, Indianápolis.

Paludo, P.H. L., Ávila, I., Moraes, A. A. U., Lindo-Samaniego, J.E., Costa, M.C. D., Pagliuso, J.D., Milioli, F.E., 2006, "Estudo de dessulfuração na planta de bancada para combustão de carvão em leito fluidizado do NETeF". Proceedings of the 11th Brazilian Congress of Thermal Sciences and Engineering - ENCIT 2006, Curitiba, Brazil.

Ramachandran, P.A., Snith, J.M. (1977), A single-pore model for gas-solid noncatalytic reactions, AIChE Journal, 23, p.353-361.

Schouten, J.C.; Van Den Bleek, C.M. (1988), The influence of oxygen-stoichiometry on desulfurization during FBC: A simple SURE modeling approach, Chemical Engineering Science, 43, p.2051-2059.

Silva Filho, C.G. da (2002). Estudo cinético-químico não isotérmico e caracterização da combustão de um carvão CE4500, 63 p. Dissertação (Mestrado) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2002.

Szekely, J.; Evans, J.W. (1970), A structural model for gas-solid reactions with a moving-boundary, Chemical Engineering Science, 25, p.1091-1107.

Szekely, J.; Evans, J.W. (1971), A structural model for gas-solid reactions with a moving-boundary II- The effect of grain size, porosity and temperatures on the reaction of porous pellets, Chemical Engineering Science, 26, p.1901-1913.

Van Houte, G.; Delmon, B. (1979), Kinetics of Reation of $CaCO_3$ with SO_2 and O_2 below 650 ^{o}C, Journal of Chemistry Society Faraday Transactions I, 75, p.1593-1605.

Wiedemann, H.G., Boller, A.; Bayer, G. (1990). Thermogravimetric studies of the reactions between dolomite and sulfur dioxide, Solid State Ionics, 43, 53-60.

Zarkanitis and Sotirchos (1989)

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