

DESULFURIZATION BY LIMESTONE IN ATMOSPHERIC BUBBLING FLUIDIZED BED COMBUSTION (ABFBC) OF COAL

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Abstract. Sulfur emission in coal power generation is a matter of great environmental concern. Limestone sorbents are widely used for reducing such emissions. Fluidized bed desulfurization by limestone sorbents is an efficient technology for sulfur removal in the combustion of fuels of high sulfur content. Besides, limestone is directly injected into the bed providing "in loco" SO₂ sorption. This work presents results from bench scale experiments on the effects of temperature, fluidization velocity (U/U_{mf}) and limestone particle sizes on SO₂ sorption in atmospheric bubbling fluidized bed combustion (ABFBC) of coal. A CE4500 energetic coal from Criciúma-SC was used, alongside with a dolomitic limestone from Ipeuna-SP. Gas concentrations were measured at the reactors exit (SO₂, O₂ and CO₂). Temperature was found to be the major parameter defining the differences in the reactive performances. At lower temperatures kinetics restrained reaction. At higher temperatures sintering and SO₂ re-emission may account for the observed lower performances. The highest conversion and sorption efficiency occurred at a temperature of 833 °C and $U/U_{mf} = 6.5$. For the present range of operational conditions the conversion, the global reaction rate coefficients and the sulfur sorption efficiency resulted, respectively, between 0.0265 and 0.0473 kmol_{SO₂}/kmol_{Ca+Mg}, 0.0171 and 0.0528 m s⁻¹, and 46.4 and 72.3 %.

Keywords: fluidized bed; desulfurization; limestone.

1. INTRODUCTION

Coals and heavy oils from petrol are widely used for energy generation. Those fossil fuels are burned in thermoelectric power stations and are the main source of SO₂ emission into the earth's atmosphere (Li and Sadakata, 1999). The development of efficient, economical and environmentally-friendly technologies is essential for the utilization of high-sulfur fuels. Fluidized bed combustion is one of such technologies. The process permits injecting limestone into the combustion chamber, sorbing SO₂ before it is emitted to the atmosphere (Baird, 1998; Kotz et al., 1994; Li and Sadakata, 1999; Van Houte and Delmon, 1979).

Bubbling fluidized bed combustion of coals is characterized by a set of complex physical and chemical phenomena. The bubbling bed regime may be considered two well defined hydrodynamic patterns: a particulate or emulsion phase characterized by gas dispersed particles, and a bubble phase characterized by gas voids with very few particles. Hence, almost all heterogeneous reactions, such as coal combustion and sulfur sorption by limestone occur in the particulate phase. The effective rates of the heterogeneous chemical reactions are controlled by mass transport and chemical kinetics. The relevant mass transfer occurs between the bubble and the particulate phases, through the particulate phase and intra-particle (Carmargo *et al.*, 2003).

Limestones are basically calcium carbonate (CaCO₃). Some rocks, also called dolomites, present significant fractions of magnesium carbonate (MgCO₃), and others are mostly double carbonate of calcium and magnesium (CaMg(CO₃)₂). When introduced into a high-temperature fluidized bed, the carbonates calcined to produce a very porous solid structure of CaO/MgO (1), which ultimately sorbs SO₂ to produce CaSO₄/MgSO₄ (2).



The actual mechanism leading to the formation of CaSO₄ is still a controversial subject among researchers. However, it is generally accepted that the reaction between the porous solid CaO and the gas SO₂ (in oxidizing atmosphere) is first-order related to SO₂ concentration. It is also agreed that the sulfation rate is maximum at temperatures around 850 °C (Allen and Hayhurst, 1996).

The products of sulfation are known to be mostly CaSO₄, CaSO₃ and CaS, and occasionally MgSO₄, MgSO₃ and MgS. Some authors affirm that only the CaO of limestone is considered a sorbent of SO_x at temperatures of interest in combustion processes, therefore the MgSO₄ formed becomes unstable at high temperatures (Weidemann and Boller, 1990; Fuertes and Fernandez, 1995). Another argument is that the reaction of MgO with SO₂ is very slow and occurs in insignificant amounts (Borgwardt and Harvey, 1972). There are also indications in literature of the occurrence of

MgSO₄ as a product of the reaction (Borgwardt, 1970). However, some results of the NETeF have shown a possible activity of MgO (Pagliuso et al., 2002).

Most works in the literature, including those by Dennis and Hayhurst (1986, 1988) and Mattisson and Lyngfelt (1998), assume calcination to be instantaneous. Hagi-Sulaiman and Scaroni (1992) performed batch experiments of sulfur sorption by limestone in a bed fluidized by pre-heated mixtures of SO₂, CO₂, O₂ and N₂. Four different limestones were used, at temperatures from 750 to 935 °C. They found that the calcination step was not instantaneous and was strongly affected by temperature, considerably affecting sulfation. The observed different behaviors of the different limestones were attributed to impurities and chemical composition. The authors observed that, impurities generally reduce the decomposition temperature and raise the initial reaction rate. They also found that some impurities affect the physical structure of the limestones during calcination.

In general, below 800 °C, chemical reactions are slow and chemical kinetics controls sulfur sorption by limestones in bubbling fluidized bed coal combustion. Between 800 and 900 °C, the chemical reaction becomes faster and mass diffusion takes control of the process. Above 900 °C, the calcium sulfate product becomes unstable and decomposes releasing SO₂. This behavior suggests there are optimal operational temperatures for which the reaction efficiency has maximum values. According to Howard (1989), in real scale plant operation under coal combustion and continuous feeding, the optimal temperature is commonly between 800 and 850 °C, where sorption of SO₂ exceeds 90 %.

Sulfur sorption by limestone in coal fluidized bed combustion has been approached by different procedures, including coal combustion (Dam-Johansen and Ostergaard, 1991; Lyngfelt and Leckner, 1989; Khan and Gibbs, 1997; Zheng et al. 1982) or experiments simulating combustion conditions (Mattisson and Lyngfelt, 1999; Dennis and Hayhurst, 1986), either in batch or continuous reaction experiments. Although experiments under coal combustion are better representatives of the real process, the unknown reactive atmosphere makes the comparison among different researches difficult. On the other hand, experiments simulating combustion conditions allow for a better control and comparability. In these cases, caution is required when evaluating results since, in general, there are considerable differences between the real processes and the simulations. Continuous experiments are usually performed in large units, while batch experiments are more commonly performed in small-scale units. While continuous experiments are more realistic, batch experiments are more flexible, allowing for the analysis of the limestone transient sorption performance (Camargo et al., 2003).

The Group of Thermal and Fluids Engineering (NETeF) of EESC-USP is running a comprehensive research program on fluidized bed combustion of Brazilian coals. The current research is directed towards coal combustion, SO₂ sorption by limestones, and fluid mechanics of gas-solid flows. The experimental research is underway in two bubbling fluidized bed plants (pilot and bench scales) and through thermogravimetry (TG). Some works in fluidized bed were realized with simulated sulfur generation in coal fluidized bed combustion. These works evaluated the effect of temperature on the conversion of sulfur sorption by limestones (Silva, 2001), the influence of different particle sizes of limestone (Silva, 2003) and the effect of SO₂ concentration on limestone sulfation (Samaniego Lindo, 2003). The first works of the group burning Brazilian coal in a bench fluidized bed reactor plant of the NETeF were developed by Michels Jr. (2004) and Costa (2005).

This work presents results from bench scale experiments on the effects of temperature and limestone particle sizes of limestone on SO₂ sorption in atmospheric bubbling fluidized bed combustion (ABFBC) of coal. The consequent variations of the exit concentrations of SO₂, O₂ and CO₂ are continuously recorded. The conversion and global reaction rate coefficient for sulfur sorption by limestone were also determined.

2. DATA REDUCTION METHODOLOGY

In the experiments of coal combustion in fluidized bed reactor, exit concentrations of combustion gases as well as entrance concentrations of fluidizing gases are measured. Among these gases are SO₂, O₂, C and CO₂. The gases concentration flowing through the bed is also measured to determine the average concentrations in the bed volume. From the measurements, the conversion and the global reaction rate coefficient were determined for the limestone sulfation.

According to Ross and Davidson (1981), the carbon in the coal is assumed to be rusted to form CO, which later rusted in fluidized medium to create CO₂. For intrinsic combustion control, it is assumed that only the O₂ concentration and the mass of fixed carbon limit the reaction rate.

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 reactions rate under external control the Fick's diffusion law is applied to describe the gases transportation in the fluidized medium (O₂ transportation toward an individual particle of coal, and SO₂ transportation toward an individual particle of limestone). For the combustion, the reaction rate under external control will be equal to the consumption rate of O₂ and for the sulfation, the reaction rate under external control will be equal to the consumption rate of SO₂ in the external surface of limestone particles.

An important parameter for the analyses of results of desulfurization is the molar ratio between calcium plus magnesium and S. The ratio (Ca+Mg)/S in the feeding of reactor is given by

$$(Ca + Mg)/S = \frac{F_A \left(\frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right)}{F_F \left(\frac{Y_S}{W_S} \right)} \quad (3)$$

The following symbols are utilized in the above equation as well as in the equations described in the following sections.

A	Bed cross sectional area, m^2
C_i^s, C_i^e	Concentration of “ i ” gas in both exit and entrance of the reactor, $kmol_i/m^3$
$C_{i,\infty}$	Concentration of “ i ” gas far from a surface of a particle, $kmol_i/m^3$
C_i^A, C_i^C	Concentration of “ i ” gas in the exit of the reactor, with or without limestone injection, $kmol_i/m^3$
F_C, F_A	Feeding rate of coal and limestone in the reactor, kg/s
K_S	Global reaction rate coefficients of sulfation, m/s
M_A	Limestone mass in the reactor in steady state operation, kg
n_A	Number of limestone particles in the reactor in steady state operation, adm
r	Particle radius, m
\mathfrak{R}_{O_2}	Reaction rate of O_2 , $kmol_{O_2} / s$
\mathfrak{R}_{SO_2}	Sorption rate of SO_2 by a limestone particle, $kmol_{SO_2} / s$
U	Superficial fluidizing velocity, m/s
W	Molecular weight, $kg/kmol$
X_S	Limestone conversion $kmol_{SO_2} \text{ sorbed} / kmol_{Ca+Mg \text{ fed}}$
Y	Mass fraction, adm
η_S	Sulfur sorption efficiency in the reactor, adm
ρ_A	Appearance density of limestone fed, kg/m^3

2.1. Desulfurization by Limestone

In the experiments in fluidized bed reactor, SO_2 concentrations are measured in the exit of the reactor. From the measurements, the parameters conversion rate and global sulfur sorption rate coefficient of limestone are determined. The limestone conversion is defined as a relation between the sorption rate of SO_2 (or of reaction of $Ca + Mg$) and the feeding rate of $(Ca + Mg)$. Thus,

$$X_S = \frac{UA(C_{SO_2}^C - C_{SO_2}^A)}{F_A \left(\frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right)} \quad (4)$$

In the case of desulfurization, it is also usual to define a removal efficiency of SO_2 in the reactor, given by

$$\eta_S = \frac{(C_{SO_2}^C - C_{SO_2}^A)}{C_{SO_2}^C} \quad (5)$$

The possibility of a reaction rate control by intrinsic or external factors, or both of them combined, is considered. Correlations can be established for the reaction rate considering each of these conditions. As in the coal combustion, the sorption rate of SO_2 by a limestone particle can be expressed as:

$$\mathfrak{R}_{SO_2} = 4\pi r^2 K_S C_{SO_2,\infty} \quad (6)$$

The sorption rate of SO_2 for all limestone particles in the bed can be obtained from

$$R_{SO_2} = UA(C_{SO_2}^C - C_{SO_2}^A) = n_A \cdot \mathfrak{R}_{SO_2} \quad (7)$$

Assuming a mean effective global reaction rate coefficient, K_s , for all limestone particles in the bed, one has

$$K_s = \frac{\rho_A r}{3M_A} UA \frac{(C_{SO_2}^C - C_{SO_2}^A)}{C_{SO_2, \infty}} \quad (8)$$

In the works of Camargo et al. (2003), Michels Jr (2004), Tureso (2004) and Costa (2005) are presented the complete deductions of the above equations.

3. EXPERIMENTAL

A CE-4500 energetic coal from Criciúma-SC was used, alongside with a dolomitic limestone from Ipeúna-SP. Table 1 shows their elementary chemical composition.

Table 1. Elementary chemical composition of coal and limestone.

Coal ⁽¹⁾		Dolomite ⁽²⁾	
Composition	% mass/mass	Composition	% mass/mass
S	5.14	Ca	17.07
O	7.93	Mg	11.73
N	0.90	Fe	0.32
H	3.52	Al	0.42
Fixed Carbon	50.59	Sr	0.08
Volatile matter	19.50	K	0.13
Residual Ash	40.66	Mn	0.09

⁽¹⁾ Silva Filho (2002); ⁽²⁾ Crnkovic (2003)

Figure 1 shows a sketch of the bench scale fluidized bed plant used in the experiments. In Paludo et al. (2006), this experimental system was presented, including the main details of construction and project of the plant, stages of tests performed, problems and solutions obtained.

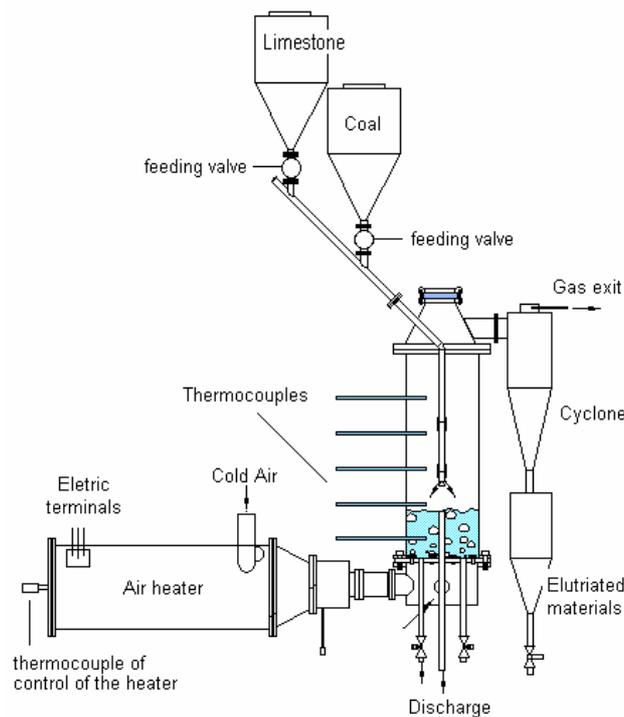


Figure 1. Sketch of the bench scale fluidized plant.



Figure 2. (a) Internal view of reactor; (b) air heater, reactor and control panel; (c) feeding valves of coal and limestone; (d) reactor out of operation; (e) and (f) reactor in operation.

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 7 and 11), temperature (between 800 and 900 °C) and particle mean size of limestone (545, 724 and 775 μm).

The mean size distribution of limestone particles of 545 and 775 μm , was obtained between two subsequent ASTM sieves. For the other particulates, i.e., silica sand (412 μm), coal (0,383 μm) and limestone particles of 724 μm , the particle size was determined using a standard set of sieves (screens) of different aperture sizes.

4. RESULTS AND DISCUSSION

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), calibration (gas analyzers, thermocouples and system of feeding of solids), etc. 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 °C and in the fluidizing velocity required. Under these conditions the coal is added into the reactor until the temperature has reached around 850 °C. Samples of the combustion gases are continuously extracted for the gas analyzers until the regimen condition has been reached. Under these conditions the limestone is added to the reactor.

Table 2 presents the data used in the calculations of the conversion and the global reaction rate coefficients.

Table 2. Data used in the equations.

m_{leito} (g)	A (m^2)	$\rho_{\text{limestone}}$ (kg m^{-3})	r (m)	Atomic or molar mass (kg kmol^{-1})			Mass Fraction (%)		
				W_{Ca}	W_{Mg}	W_{S}	Y_{Ca}	Y_{Mg}	Y_{S}
942.74	0.0201	2,850	0.000359	40.08	24.31	32.1	0.1707	0.1173	0.0235

Figure 3 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 observed that, initially there are high concentrations of SO_2

and after adding limestone into the reactor the concentration decreases.

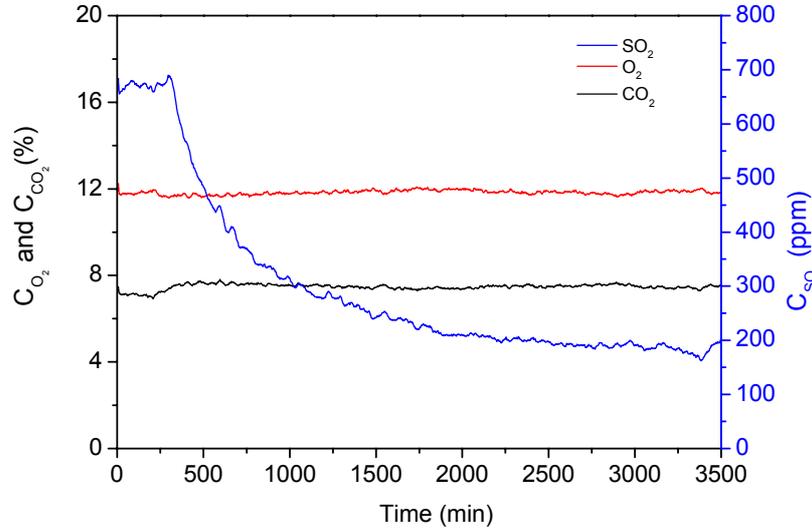


Figure 3. Exit transient concentration profiles of O_2 (C_{O_2}), CO_2 (C_{CO_2}) and SO_2 (C_{SO_2}) as a function of time (t).

The following results were obtained in ten tests, all with the same behavior showed in Fig. 3. In all tests some parameters varied: U/U_{mf} , temperature and particle mean size of limestone. Table 3 presents the parameters and results of all tests.

Table 3. Tests of desulfurization by limestones executed in ABFBC.

Parameters and Results	Experiments									
	01	02	03	04	05	06	07	08	09	10
Particle Size (μm)	724	724	724	545	545	775	775	775	775	724
F_C (g/s)	0.350	0.350	0.434	0.561	0.434	0.383	0.392	0.476	0.451	0.595
F_A (g/s)	0.176	0.176	0.215	0.294	0.294	0.201	0.201	0.233	0.222	0.316
Ratio (Ca+Mg)/S	6.25	6.25	6.12	6.50	8.39	6.50	6.36	6.05	6.10	6.58
T_m ($^{\circ}C$)	833	800	800	870	887	812	852	851	807	836
U (m/s)	0.779	0.811	1.053	1.169	0.858	0.801	0.841	1.143	1.126	1.174
U_{mf} (m/s)	0.119	0.122	0.122	0.116	0.114	0.121	0.117	0.117	0.121	0.109
U/U_{mf} (ms)	6.5	6.6	8.6	10.1	7.5	6.6	7.2	9.7	9.3	10.8
C_{sc} (ppm)	672.1	497.6	447.3	633.0	729.7	647.1	653.4	567.6	585.9	736.9
C_{cc} (ppm)	186.3	235.1	190.9	312.2	297.1	274.8	350.3	303.8	267.4	250.0
η_S (%)	72.3	52.7	57.3	50.7	59.3	57.5	46.4	46.5	54.42	66.1
X_S (kmol $_{SO_2}$ /Kmol $_{Ca+Mg}$)	0.0473	0.0274	0.0286	0.0272	0.0265	0.0332	0.0274	0.0280	0.0363	0.0396
K_S (m/s)	0.0444	0.0198	0.0313	0.0193	0.0171	0.0247	0.0168	0.0237	0.0319	0.0528

In the present experiments the sulfation rate was significantly affected by fluidization velocity, process temperature and particle mean size. This was quite expected since fluidization velocity defines gas residence time and mass transfer conditions in the bed, temperature defines kinetics resistance to reaction and particle size defines the surface area available for reaction.

Other important variables that could also significantly affect sulfation rate are the (Ca+Mg)/S molar feeding ratio and the concentration of SO_2 in the reacting atmosphere. For dolomitic limestone, both Tureso (2005) and Costa (2005) showed that (Ca+Mg)/S molar feeding ratios above 4 have little effect on conversion. In the present experiments the (Ca+Mg)/S molar feeding ratio was always higher than 4 (between 6.05 and 8.39), so that this parameter did not significantly affect conversion. Samaniego Lindo (2003) performed batch experiments on the sulfation of dolomitic limestone in atmospheres with different concentrations of SO_2 . In the range of solid residence times of the present experiments (1000 to 1800 seconds), Samaniego Lindo applied time averaged concentrations of SO_2 from about 50 up to about 2300 ppm. The data of the author show that averaged concentrations of SO_2 from about 50 to about 450 ppm do not significantly affect conversion. In the present experiments the SO_2 concentration in the bed was between 186 and 350 ppm, so that this parameter did not significantly affect conversion.

Figures 4, 5 and 6 show the global reaction rate coefficient, the conversion and the sorption efficiency for the various experiments, as a function of the process temperature. In order to allow for a better evaluation of the results, the various cases are grouped in to three different classes, namely I (experiments 1 and 10), II (experiments 2, 3, 6 and 9) and III (experiments 4, 5, 7 and 8). Class I comprises the cases in which the highest sulfation performances were observed. Classes II and III comprise cases of lower performances.

Temperature was found to be the major parameter defining differences on reactive performances. The experiments of class II were less effective than those of class I. The relatively lower temperatures of the experiments in class II, meaning slower kinetics, account for that. Differences in particle size and fluidization velocity can be disregarded as possible causes for the lower performances of class II, since inside classes I and II there are cases with particulate diameter and fluidization velocities which are either equal or very close.

The experiments of class III also were less effective than those of class I, despite their relatively higher temperatures and consequently faster kinetics. Sintering on the reaction surfaces and SO₂ re-emission may account for that. Also here, differences in particle size and fluidization velocity can be disregarded as possible causes for the lower performances of class III, since inside classes I and III there are cases with particulate diameter and fluidization velocities which are either equal or very close.

Inside class I, case 10 presented lower conversion and sorption efficiency than case 1. Those cases are very similar, except for the fluidization velocity, which is much higher for case 10. Therefore, the lower performance of case 10 is clearly due to a lower gas residence time in the bed. Otherwise, the global reaction rate coefficient of case 10 resulted higher than that for case 1 since the global rate coefficient is directly proportional to the fluidization velocity (see Equation 8).

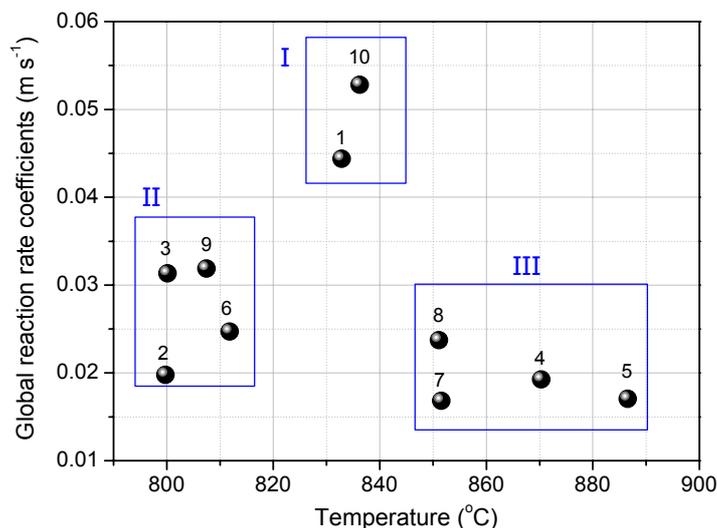


Figure 4. Global reaction rate coefficient as a function of the temperature for the various experiments.

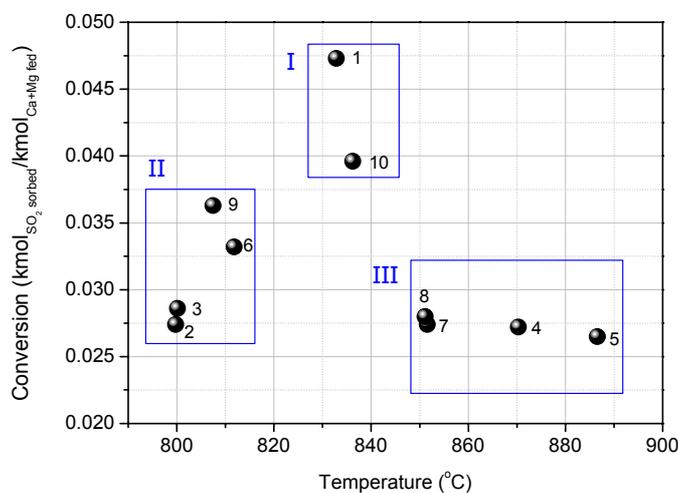


Figure 5. Conversion as a function of the temperature for the various experiments.

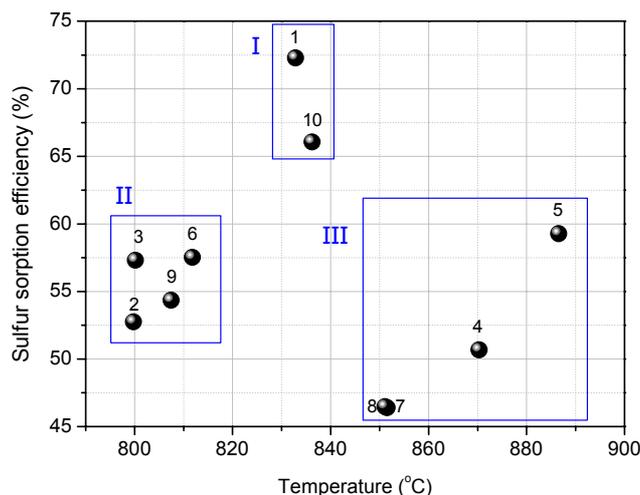


Figure 6. Sorption efficiency as a function of the temperature for the various experiments.

Figure 7 shows a complementary test with a limestone of 724 μm , to evaluate the sintering of the limestone or re-emission of SO_2 at high temperatures. The sorption of SO_2 for the limestone was expected to stabilize and then initiate a rise in temperature of up to 950 $^\circ\text{C}$. Figure 7 clearly shows that the SO_2 concentration increased when the temperature was higher, evidencing the sintering or re-emission.

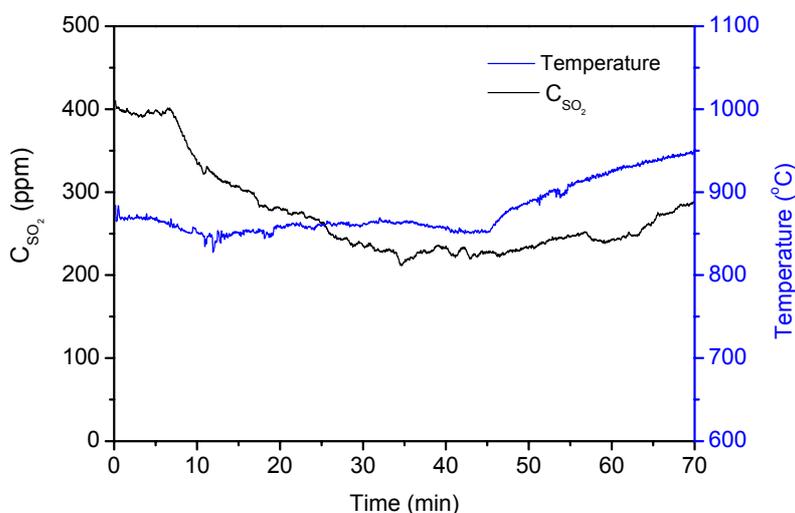


Figure 7. Exit transient concentrations profiles of SO_2 (C_{SO_2}) as a function of time. Re-emission or sinterization of limestone is observed at high temperatures.

5. CONCLUSIONS

Conversion, sorption efficiency and global reaction rate coefficients on limestone sulfation were determined in a fluidized bed burning coal. Different operational conditions were considered in ten experiments, in which the sulfation rate was significantly affected by fluidization velocity, process temperature and particle mean size.

For the considered range of operational conditions, temperature was found to be the major parameter defining the differences in the reactive performances. At relatively lower temperatures, slower kinetics restrained reaction. At higher temperatures sintering or SO_2 re-emission reduced sulfation performances.

The highest conversion and sorption efficiency occurred in those cases where the gas residence time in the bed was higher. In all of the experiments lower sorption efficiencies were found since the gas residence time in the bed was not enough to allow for higher SO_2 removals from the gas.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

- Allen, D. and Hayhurst, A.N., 1996, “Kinetics of the reaction between gaseous sulfur trioxide and solid calcium oxide”, *J. Chem. Soc. Faraday Trans.*, Vol. 92, No. 7, pp.1239-1242.
- Avedesian, M. M. and Davidson, J. F., 1973, “Combustion of carbon particles in a fluidised bed”, *Trans. Inst. Chem. Engrs.*, Vol. 51, pp.121-131.
- Baird, C., 1998, “Environmental Chemistry”, 2nd ed., W.H. Freeman and Company: New York.
- Borgwardt, R. H. and Harvey, R. D., 1972, “Properties of carbonate rocks to SO₂ reactivity”, *Env. Sc. Tech.*, No. 6, pp.350-360.
- Borgwardt, R.H., 1970, “Kinetics of the reaction of SO₂ with calcined limestone”. *Environ. Sci. Technol.*, Vol. 4, No.1, pp.59-63.
- Camargo F.L., Pagliuso, J.D., Milioli, F.E., 2003, “Conversion and global reaction rate coefficient in the absorption of SO₂ by different types of limestone in a fluidized bed reactor”, *Engenharia Térmica*, No. 3, pp.50-57.
- Costa, M.C.D., 2005, “Emissões poluentes na combustão em leitos fluidizados de carvão mineral”, PhD Thesis, 114p., University of São Paulo, Engineering School of São Carlos, Brazil.
- Crnkovic, P. C. G. M., 2003, “Análise Termogravimétrica para a Determinação de Fatores que Afetam a Eficiência de Sorção de SO₂ por Calcários na Combustão de Carvões”, PhD Thesis, 127p., University of São Paulo, Institute Of Chemistry of São Carlos, Brazil.
- Dam-Johansen, K. and Ostergaard, K., 1991, “High-temperature reaction between sulphur dioxide and limestone – I. Comparison of limestones in two laboratory reactors and a pilot plant”, *Chemical Engineering Science*, Vol. 46, No. 3, pp.827-837.
- Dam-Johansen, K. and Ostergaard, K., 1991, “High-temperature reaction between sulphur dioxide and limestone – II. An improved experimental basis for a mathematical model”, *Chemical Engineering Science*, Vol. 46, No.3, pp.839-845.
- Dam-Johansen, K. and Ostergaard, K., 1991, “High-temperature reaction between sulphur dioxide and limestone – III. A grain-micrograin model and its verification”, *Chemical Engineering Science*, Vol. 46, No. 3, pp.847-853.
- Dam-Johansen, K. and Ostergaard, K., 1991, “High-temperature reaction between sulphur dioxide and limestone – IV. A discussion of chemical reaction mechanisms and kinetics”, *Chemical Engineering Science*, Vol. 46, No. 3, pp.855-859.
- Dennis, J.F. and Hayhurst, A.N., 1986, “A Simplified analytical model for the rate of reaction of SO₂ with limestone particles”, *Chemical Engineering Science*, Vol. 41, No. 1, pp.25-36.
- Dennis, J.F. and Hayhurst, A.N., 1988, “The formation of SO₃ in a fluidised bed”, *Combustion and Flame*, Vol. 72, pp.241-258.
- Fuertes, A.B., Fernandez, M.J., 1995, “Kinetics of the calcium sulfate decomposition”. *Trans. IChemE*, Vol. 73, Part A.
- Haji-Sulaiman, M.Z. and Scaroni, A.W., 1992, “The rate limiting step in the sulfation of natural limestones during fluidized bed coal combustion”, *Fuel Processing Technology*, Vol. 31, pp.193-208.
- Howard, J. R., 1989, “Fluidized bed technology: principles and applications”. New York, Adam Hilger, 214 p.
- Khan, W.Z., Gibbs, B.M., 1997, “Reduction of SO_x emissions from a fluidized bed under staged combustion by fine limestone”, *Enviroment International*, Vol. 23, No. 2, pp. 227-236.
- Kotz, J.C.; Joesten, M.D.; Wood, J.L. & Moore, J.W., 1994, “The chemical world – concepts and applications”, Harcourt Brace & Company, Orlando, 954p.
- Li, Y. and Sadakata, M., 1999, “Study of Gypsum Formation of Appropriate Dry Desulfurization Process of Flue Gas”, *Fuel*, No. 78, pp.1089-1095.
- Lyngfelt, A. and Leckner, B., 1989, “SO₂ capture in fluidized-bed boilers: re-emission of SO₂ due to reduction of CaSO₄”, *Chemical Engineering Science*, Vol. 44, No. 2, pp.207-13.
- Mattisson, T. and Lyngfelt, A., 1999, “The reaction between limestone and SO₂ under periodically changing oxidizing and reducing conditions - effect of temperature and limestone type”, *Thermochimica Acta*, Vol. 325, pp.59-67.
- Mattisson, T.; Lyngfelt, A., 1998, “Reaction between sulfur dioxide and limestone under periodically changing oxidizing and reducing”. *Energy Fuels*, Vol. 12, pp.905-912.
- Michels Jr., V., 2004, “Influência da temperatura na absorção de SO₂ por calcários na combustão em leito fluidizado de carvão mineral”, MSc Dissertation, 111p, University of São Paulo, School of Engineering of São Carlos, Brazil.
- 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.
- Ross, I. B. and Davidson, J. F., 1981, "The combustion of carbon particles in a fluidised bed", *Trans. Inst. Chem. Engrs.*, Vol. 59, pp. 108-114.
- Samaniego Lindo, J.E.S., 2003, "Efeito da concentração de SO₂ nas reações de calcinação e sulfatação de calcários em reator de leito fluidizado", MSc Dissertation, 116p., University of São Paulo, Engineering School of São Carlos, Brazil.
- Silva Filho, C.G. da, 2002, "Estudo cinético-químico não isotérmico e caracterização da combustão de um carvão CE4500", MSc Dissertation, 63p., University of São Paulo, Engineering School of São Carlos, Brazil.
- Silva, G.F. da, 2001, "Efeito do tamanho médio de particulado sobre a conversão e o coeficiente global de taxa de reação na absorção de SO₂ por calcário em reator de leito fluidizado", MSc Dissertation, 79p, University of São Paulo, Engineering School of São Carlos, Brazil.
- Tureso, J. P., 2004, "Estudo de uma Planta Piloto para a Combustão em Leito Fluidizado de Carvões Mineraiis Brasileiros", PhD Thesis, 118 p, University of São Paulo, Engineering School of São Carlos, Brazil.
- Van Houte, G. and Delmon, B., 1979, "Kinetics of reaction of CaCO₃ with SO₂ and O₂ below 650 °C", *J. Chem. Soc. Faraday Trans. I.*, No. 75, pp. 1593-1605.
- Weidemann H.G., Boller, A., 1990, "Thermogravimetric studies of the reactions between dolomite and sulfur dioxide", *Solid State Ionics*, v.43, p.53-60.
- Zheng, J., Yates, J.G. and Rowe, P.N., 1982, "A model for desulphurisation with limestone in a fluidised coal combustor", *Chemical Engineering Science*, Vol. 37, no. 2, pp.167-174.

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