Desulfurization kinetics of coal combustion gases

S.R.Bragança[I, *]; A.Jablonski[I]; J.L.Castellan[II]

[I]Universidade Federal do Rio Grande do Sul, UFRGS, Av. Osvaldo Aranha 99/705, 90040 - 010, Porto Alegre - RS, Brazil. E-mail: saulorb@ufrgs.br
[II]Fundação de Ciência e Tecnologia, CIENTEC, R. Washington Luiz, 675, Cx.P.1864, 90010 - 460, Porto Alegre - RS, Brazil

---

ABSTRACT

Desulfurization of the gases from coal combustion was studied, using limestone (marble) as the sorbent in a fluidized-bed reactor. The kinetic parameter, k, was measured by analyzing the reduction in SO_2 emissions in relation to time when a batch of limestone was introduced directly into the combustor chamber. The influence of sorbent composition and particle size was also studied. The CaO content in the limestone was more important than the MgO content. Sorbent particle size showed a strong influence on the reaction time and efficiency of desulfurization. The results of this work prove that marble type is very important in the choice of sorbent for a desulfurization process. A magnesian limestone showed a better performance than a dolomite. Therefore, the magnesian limestone is more efficient for a shorter particle residence time, which is characteristic of the bubbling fluidized bed.

Keywords: desulfurization kinetics, limestone, coal, fluidized bed.

INTRODUCTION

This work was part of a project to study control of sulfur emissions deriving from the combustion of high-ash coal in the southern region of Brazil. This coal is very abundant but it has been underutilized. Since industry in the region is growing very fast, high ash-coal is a promising source of energy. The use of natural gas and the construction of hydroelectric plants do not seem to be sufficient or economically attractive.

Currently the generation of electric power from coal combustion in the state of Rio Grande do Sul is approximately 500 MW. The main power plant is the Presidente Médici thermoelectric plant, which is using old technology without flue gas treatment. An increase in coal consumption requires implementation of actions able to minimize emissions of polluted gas to prevent the formation of acid rain. New power stations need to use clean technologies, such as the circulating fluidized bed or a flue gas cleaning system, in agreement with worldwide tendencies. These technologies must considerably reduce SOx and NOx emissions, which are the main ones responsible for the formation of acid rain.

The fluidized bed is suitable for burning high-ash coal with a high combustion efficiency. The relatively low combustion temperature (850°C) produces a lower level of NOx emissions than the temperature in the pulverized coal combustor (1200°C). SOx emissions can be reduced by introducing limestone directly into the combustor chamber, which is very attractive due to the low cost of limestone and its availability near coal mines.

Southern Brazil has large deposits of coal and limestone. However, their physical and chemical properties are very specific. As a consequence, the use of technology from abroad in the recent past has failed.

Coal from the Candiota mine is sub-bituminous with a high level of ash of around 50% and a low calorific value. However, this coal is low in sulfur and is highly reactive, thus making its utilization more interesting. In addition, the price of Candiota coal is very low (US$ 8-10/ton). Limestone is actually a marble or a metamorphic rock, since it has undergone a metamorphic process. This has produced different rock characteristics, such as low porosity and low friability. However, porosity increases considerably calcination, which makes marble a very efficient desulfurization material.

The use of limestone to reduce SOx emissions has been studied in the last few decades. There are a lot of systems to prevent the emission of SOx gases, and they are economic and technologically acceptable. Examples of these are scrubbers and the spray drier. Introduction of limestone into the furnace is inefficient for combustors that use a high combustion temperature, such as pulverized coal combustor system (Slack and Falkenberry, 1970). The fluidized-bed reactor is a technology that has a high rate of mass and heat transfer, and it has proved to be effective by a lot of published research (Renz, 1981; Valk, 1995). Fluidized beds offer more advantages than older technologies when using limestone. The energy capacity of the fluidized bed has improved a lot recently, and power generation plants of 350 MW have already been built (Makansi, 1994).

The sulfation reaction is a two-step reaction. First, the decomposition of carbonate occurs, producing calcium oxide. Then the CaO reacts with sulfur dioxide forming sulfate. This reaction is called "sulfation"; it is a first-order, gas-solid reaction that produces a solid product,

$$CaO_{(s)} + SO_{2(g)} + 1/2\ O_{2(g)} \rightarrow CaSO_{4(s)}$$
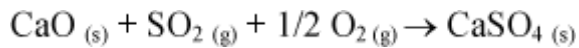
The sulfation reaction rate is strongly influenced by sorbent particle size. Sorbent of a smaller size is more highly reactive. By increasing the particle size of the sorbent, the main resistance to the reaction changes from pore diffusion and surface reaction to diffusion through the $CaSO_4$ product layer formed on the particle surface of the sorbent (at a given thickness, solid-state diffusion becomes rate-controlling). Consequently, the $CaSO_4$ layer causes pore blockage which prevents sulfation of the inner parts of the particles, diminishing the maximum conversion of the sorbents. Particle size is the most important parameter for characterization of the sorbent (Adánez et al., 1994). Munzel et al. (in: Valk, 1995) showed by their laboratory tests that the best results are obtained with either extremely fine limestone particles (large surface area) or limestone particles with a diameter just larger than the elutriation size (lower surface area, but longer residence time).

Limestone with a high $MgCO_3$ content has a specific grain structure for the calcined material, which means a larger pore surface area and thus a greater potential for calcium utilization. However, a higher $MgCO_3$ content, as occurs in dolomite, requires a larger volume of sorbent to obtain the same Ca/S molar ratio from calcitic and magnesian limestones. As a consequence, the use of dolomite generates more solid waste resulting in some losses of energy (Martin, 1981).

The physical properties of the parent rocks can not be easily related to the SO_2 retention capacity of the limestones. After calcination, the CaO generated has a structure which is completely different from that of the parent rock. The structure of the CaO is a consequence of the properties of the parent rock and the experimental conditions – temperature and CO_2 and H_2O content in the reaction atmosphere, etc. (Sotirchos and Zarcantis, 1992). Thus, properties such as porosity, BET surface area and resistance to attrition are important characteristics of the CaO formed, but may not be important in the limestone, since the calcination reaction is very fast (Davini, 2000).

According to Adánez et al. (2001), the calcination of limestone particles can be assumed to occur instantaneously. The kinetics of the sulfation reaction are determined by reactivity of the sorbent. In addition, the sulfation reaction rate depends on the SO_2 concentration around the particles and on the mean residence time of the particles in the bed.

In this paper, some kinetic aspects of gas desulfurization were studied using marble as the sorbent and high-ash coal as the fuel. Types of marbles from two different regions were compared because of their different properties and chemical compositions. In a fluidized-bed reactor a portion of marble (150g or 500g) was put directly in the combustor chamber, keeping the coal flow unchanged (2 kg/h).

The SOx emissions were continuously monitored by an infrared analyzer to observe how long the marble has to react until a minimum level of SOx emissions is reached, and how long it continues reacting in the system. The data presented in this work is considered to be very useful for reactor design.

MATERIALS AND METHODS

Two types of marble from different mines were used in this study, a dolomite (high $MgCO_3$ content) from the Pantano Grande region and a magnesian limestone (low $MgCO_3$ content) from the Candiota region. They were classified according to the nomenclature suggested by Pettijohn (1957), and different mean particle sizes were used. The properties of these types of marble are shown in Tables 1 and 2.

Table 1: Marble properties.

Sample	Mineralogy	CaO (%)	MgO (%)	Mean particle size (mm)	BET surface area (m^2/g)	Apparent porosity (%)
Magnesian limestone	serpentine marble	45	2	0.42	0.57	0.36
				1.32	0.22	-
Dolomite	serpentine marble	31	22	0.22	9.95	-
				0.35	9.54	6.22

Table 2: Marble particle size distribution.

Sieve size (mm)	Dolomite (mass %)	Magnesian limestone (mass %)
-1 + 0.85	6.2	0
-0.85 + 0.5	15.2	27.1
-0.5 + 0.25	53.0	71.0
-0.25 +0.18	16.6	0.35
-0.18 + 0.15	5.6	0.2
-0.15 + 0.075	3.4	1.3
mean (mm)	0.35	0.42

Tables 1 and 2 show that there was a slight difference between the mean particle size (calculated using Sauter's formula, given in Pacheco, 1992) and the particle size distribution of the 0.42 mm magnesian limestone and the 0.35 mm dolomite. The authors assumed that this difference would not have a significant influence on the comparative analysis of the chemical compositions. It must also be highlighted that the magnesian limestone has a higher CaO content than the dolomite. Therefore, as the same amount of marble was used in the tests (a batch of 150g), allowing analysis of the influence of different contents of CaO and MgO on SO_2 emissions, the data can not be correlated with the Ca/S molar ratio. The influence of the Ca/S molar ratio on SO_2 emissions was presented in another paper (Bragança et al., 1999).

It can be seen in Table 1 that the dolomite has a higher BET surface area and a higher apparent porosity (analyzed by mercury intrusion) than the magnesian limestone. The influence of these parameters will be analyzed in this study.

The minimum fluidizing velocity of the materials is shown in Table 3. The fluidizing velocity of air is 68 cm/s (Table 5). Therefore, only the 1.32 mm magnesian

limestone has a minimum fluidizing velocity higher than that of fluidizing air, which should result in poor fluidization. The other marble particle sizes were in agreement with the Levenspiel and Kunii's recommendations (1991).

Table 3: Minimum fluidizing velocity.

Material (mean particle size)	U mf (cm/s)
Coal 0.74 mm	29.7
Magnesian limestone 0.42 mm	19.1
Magnesian limestone 1.32 mm	87.9
Dolomite 0.22 mm	5.6
Dolomite 0.35 mm	14.2

Table 4: Candiota coal properties.

	Candiota coal
Proximate analysis	
Fixed carbon (%)	25.1
Volatile matter (%)	18.7
Ash (%)	56.2
Ultimate analysis	
Carbon (%)	31.6
Hydrogen (%)	2.13
Oxygen (%)	8.3
Nitrogen (%)	0.68
Sulphur (%)	1.13
Moisture (%)	11.7
Gross C.V. (kcal/kg)	2835

Table 5: Experimental conditions.

Parameters	
Bed temperature	850°C +/- 15°C
Bed initial material	Sand
Area of the cross-section	177 cm^2
Expanded bed height	35 cm
Static bed height	16 cm
Gas residence time	0.6 s
Fluidizing air flow	21 kg/h
Fluidizing air velocity	67 cm/s
Excess air	180 %
Coal flow	2 kg/h
O_2 in flue gas	12 %

The terminal velocity for a 0.016 mm dolomite is 74 cm/s, which is higher than the fluidizing velocity of air, which results in the elutriation of the sorbent. However, a particle size of 0.016 mm is much finer than the mean particle size of the materials used in this study. As a consequence, elutriation of the materials was not expected to be significant and the residence time had to be long enough for the sulfation reaction to occur.

The coal used was from the Candiota mine, which is located in the region where the magnesian marble is from. This coal mine is an open pit mine which does not require a coal washing process. Consequently, the low cost of extraction and beneficiation compensates for the poor calorific value and the high ash content of the Candiota coal. Table 4 shows the composition of the coal.

A scheme of the fluidized-bed reactor is shown in Fig.1, and the experimental conditions are summarized in Table 5.
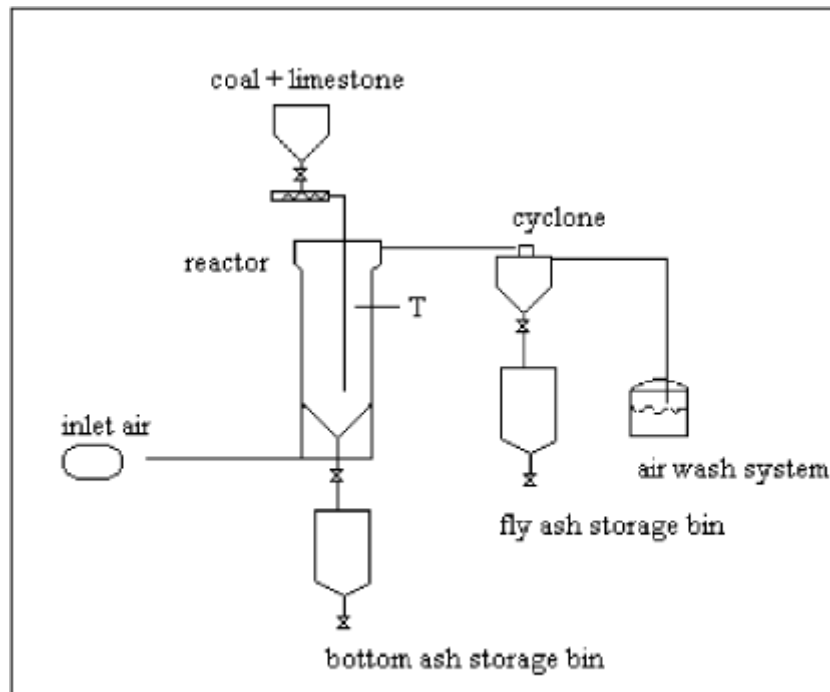

Figure 1: Reactor scheme.

Gas emissions were monitored by an infrared continuous Analyzer (MIR 9000 - *Émission S.A.*).

Batch experiments were performed for analysis of the kinetic parameter. The level of SOx emissions was recorded after the bed temperature reached 850°C and SOx emissions became stable. Then a batch of marble (150g) was introduced directly into the combustion chamber for each test. Coal feed was kept unchanged (2 kg/h).

SOx emissions decreased sharply with the addition of marble, which also caused a drop in temperature of approximately 50°C in the bed. However, the temperature quickly returned to the initial level with good reproducibility of the tests.

The time spent to reach the minimum level of SOx emissions and the time required to return to the initial point were recorded. Parameter K was calculated by data logarithmical linearization from the slope of the curve for SO_2 (log ppm) × time(s).

RESULTS AND DISCUSSIONS

Fig. 2 shows a comparison of the types of marble used as desulfurization material in the batch experiments. The same sorbent particle distribution size could not be used in the tests due to the different origins of the marble, but the authors believe that this difference is not large enough to have a negative influence on test reliability. The results showed that the magnesian limestone had a better performance, even with a particle size slightly larger than that of dolomite (Fig.2).
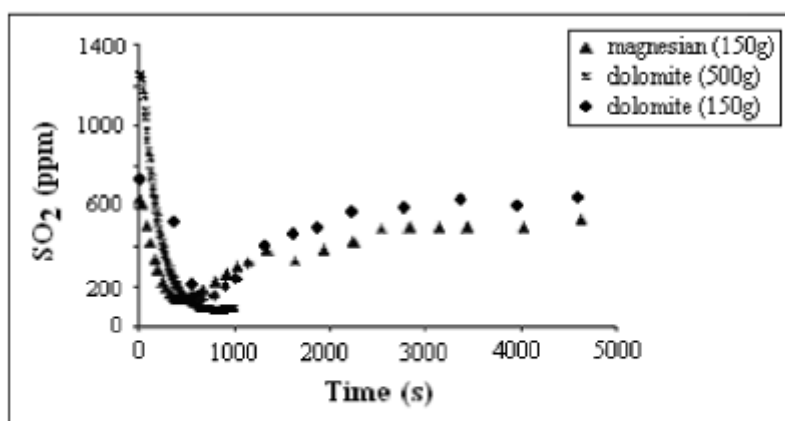

Figure 2: Effect of chemical composition and batch quantity of sorbent on SO_2 emissions. Magnesian limestone (0.42 mm) and dolomite (0.35 mm). T = 850 °C. Sorbent batches of 150g and 500g.

The 0.42 mm magnesian limestone (150g) required 7.3 minutes to reach 78% of desulfurization and the minimum level of SO_2 emissions (139 ppm). The 0.35 mm dolomite (150g) reached approximately the same level of SO_2 emissions (131 ppm) in 11 minutes, with a desulfurization efficiency of 82%. In 12.8 minutes the 0.35 mm dolomite (500g) reached 96.3% desulfurization, which corresponds to the lowest emission of SO_2 (80 ppm). This dolomite (500g) needed to reach 80% desulfurization in only 5.8 minutes.

Analysis of the results obtained with the same amount of marble (150g) showed that the magnesian limestone (67.2g of CaO and 3g of MgO) was better for retention of sulfur dioxide (Fig. 2). The magnesian limestone was faster and reached the same desulfurization efficiency as the dolomite (47g of CaO and 32.5g of MgO). This can be explained by the higher CaO concentration in the bed, when the magnesian limestone was used, independently of MgO concentration. Therefore, the higher concentration of CaO governed the kinetics of the process. This was also obtained in the 500g dolomite test (157g of CaO and 108g of MgO).

To verify the effect of particle size, samples of marbles with the same chemical composition were compared (Figs. 3 and 4). The 1.32 mm magnesian limestone reached 53.7% desulfurization in 7.3 minutes and then slower down, showing lower levels of desulfurization than the 0.42 mm magnesian limestone (78% desulfurization in 7.3 minutes). The 0.22 mm dolomite (Fig. 4) reached only an intermediate level of desulfurization efficiency (65.4%), i.e. 227 ppm of SO_2 emissions, the minimum level for this material, was reached in 8 minutes. Therefore, the performance of the 0.22 mm dolomite was worse than that of the 0.35 mm dolomite (11 minutes, but with 82% desulfurization).
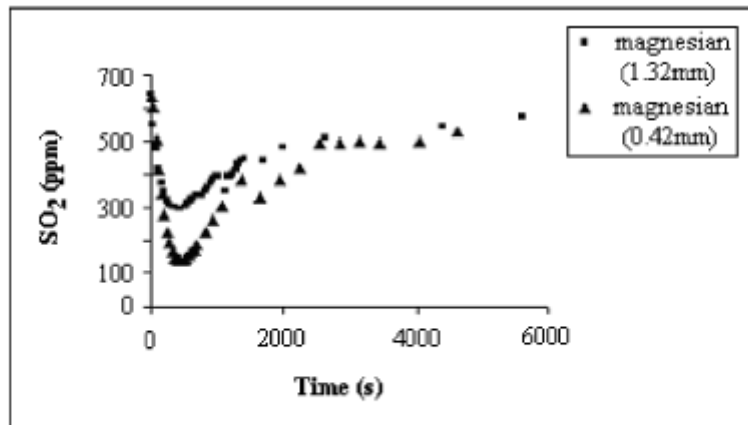

Figure 3: Effect of sorbent particle size on SO2 emissions. Magnesian limestone particle sizes of 0.42 mm and 1.32 mm. T = 850 °C. Sorbent batch of 150g.
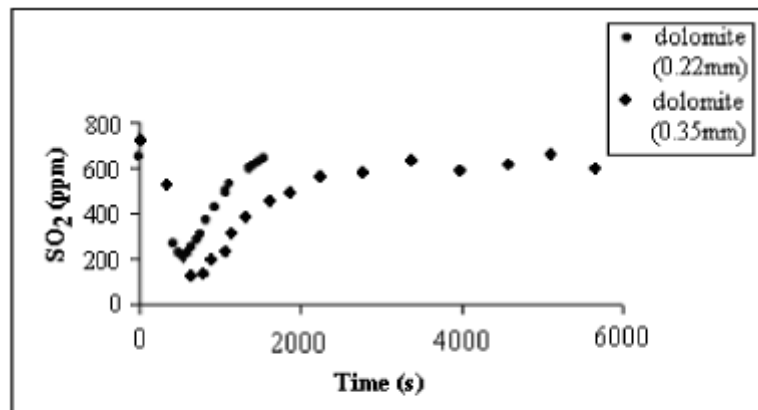

Figure 4: Effect of sorbent particle size on SO_2 emissions. Dolomite particle sizes of 0.35 mm and 0.22 mm. T = 850 °C. Sorbent batch of 150g.

The fluidization conditions such as mixture of the materials in the bed, elutriation of the materials, and residence time can explain the behavior of the marble in this study.

The 0.22 mm dolomite was faster than the 0.35 mm dolomite at the beginning of the process due to the larger surface area of the 0.22 mm dolomite particles. On the other hand, these particles had a shorter residence time. Consequently, the 0.22 mm dolomite could not achieve the same desulfurization efficiency as the dolomite 0.35 mm (considering the time required to reach the minimum level of SO_2 emissions). Thus, residence time is more important that a relatively larger surface area. This means that a portion of the 0.22 mm dolomite sample was elutriated before the reaction was completed. This result disagrees with Munzel's proposal (in Valk, 1995), which suggests the use of a sorbent with a very small particle size.

It could be also expected that a higher desulfurization efficiency would be achieved with the 1.31 mm magnesian limestone, even if more time were required. However, the 1.32 mm magnesian limestone didn't have good fluidization (as predicted according to the minimum calculated fluidizing velocity shown in Table 3) and was probably segregated in the reactor. Thus, a higher particle size than that recommended based on the theoretical calculation of fluidization must be avoided in the flue gas desulfurization process.

For calculation of the kinetic parameter (Fig. 5), several assumptions were made. The marble was the excess reagent, but for technical reasons, were continuously measured SO_2 emissions, which decreased as the sulfation reaction proceeded. Thus, the order of reaction was assumed to be 1 (Hsia et al., 1993). The sulfur content of the coal did not change during the test. The small changes in experimental conditions such as bed temperature and excess air from one run to another were disregarded. The rate of desulfurization was higher at the beginning of the test than it was at the end. Thus, considering the entire range of time, parameter K decreased during the test, and this is reflected by a change in the slope of the line (SO_2 log ppm / time). However, for a comparative analysis, it was assumed to be insignificant. Despite these assumptions, the authors considered the data reliable and surely closer to industrial reality than perfect kinetic conditions such as thermogravimetric analysis.
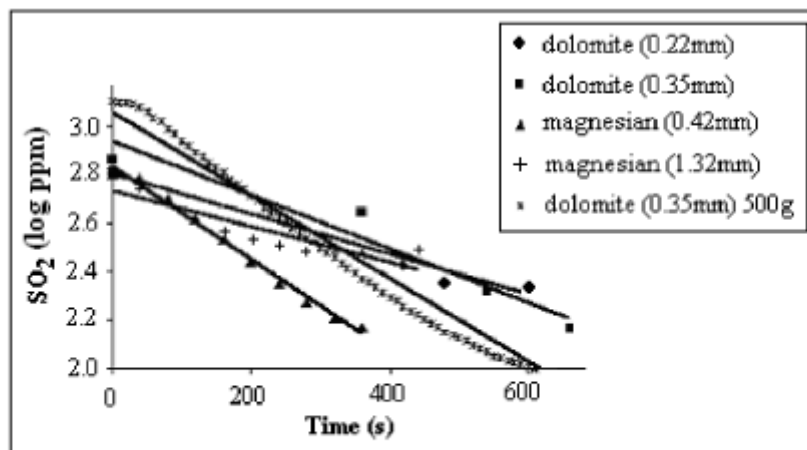

Figure 5: Analysis of reaction rate. Magnesian limestone (0.42 mm and 1.32 mm) and dolomite (0.35 mm and 0.22 mm). T = 850 °C. Sorbent batches of 150g and 500g.

The data shown in Fig. 5 and Table 6 are in agreement with the results discussed above. It must be noted that the larger BET surface areas for dolomite marble (shown in Table 1) did not have any positive effect on desulfurization. Thus, the BET surface areas of the calcined materials were calculated.

Table 6: Kinetic parameter (k).

Material	Kinetic parameter "k" (s^{-1})
Magnesian limestone 1.32 mm (150g)	-12.10^{-4}
Magnesian limestone 0.42 mm (150g)	-18.10^{-4}
Dolomite 0.35 mm (150g)	-11.10^{-4}
Dolomite 0.22 mm (150g)	-8.10^{-4}
Dolomite 0.35 mm (500g)	-22.10^{-4}

The BET surface areas of the calcined dolomite and the calcined magnesian limestone were 14.0 m^2/g and 6.7 m^2/g, respectively, at the same marble particle size (0.44 mm). As can be seen, a significant decrease in the difference in surface areas was obtained with the calcined materials, when compared to the data in Table 1 (for raw materials). These materials were calcined in a muffle furnace. Under the experimental conditions in a fluidized-bed reactor, a calcined material may have different surface areas. It can be concluded that the surface area of a raw material should not be correlated with a desulfurization process, as the results of this study show.

CONCLUSIONS

Analysis of the influence of the chemical composition of marble on the kinetics of the desulfurization process showed that the magnesian marble had a better performance than the dolomite. Both reached a high level of desulfurization of around 80%, but the magnesian limestone was faster. This behavior can be explained by the higher CaO content of the magnesian limestone. Thus, the results of these tests point to the importance of CaO concentration in the bed, independently of the MgO concentration.

Experiments with samples of marble having the same chemical composition but different particle sizes were performed. The 1.32 mm magnesian limestone (a lower surface areas but a higher residence time) reacted more slowly and reached a lower level of desulfurization than the 0.42 mm magnesian. The 0.22 mm dolomite (a higher surface areas but a lower residence time) had a lower desulfurization efficiency than the 0.35 mm dolomite. These tests prove that the choice of sorbent particle size must be balanced with residence time and fluidization conditions, i.e., there must be a good gas-solid mixture in the reactor. Therefore, the kinetics of the sulfation reaction is not fast enough to compensate for the shorter residence time of the 0.22 mm dolomite. On the other hand, the low efficiency of the 1.32 mm magnesian limestone is explained by the poor mixing of this material in the bed, and this proves that particle size must meet the requirements of the theoretical calculations for fluidization.

From the experimental results, it can be concluded that the desulfurization efficiency must not be correlated with marble (raw material) surface area. The calcined material has a surface area which is different from that of the raw materials, and the value of the surface area formed under coal combustion conditions is difficult to predict. The magnesian limestone calcined in a muffle furnace had a surface area ten times larger than of the magnesian raw material.

NOMENCLATURE

k　　Kinetic parameter

REFERENCES

Adánez, J. and Cabanillas, A., Methods for Characterization of Sorbents Used in FBC, Fuel, vol. 73, no. 3, pp. 355-362 (1994).　　[Links]

Adánez, J., Gayán, P., Grasa, P., Diego, L.F., Armesto, L. and Cabanillas, A. Circulating Fluidized Bed Combustion in the Turbulent Regime: Modelling of Carbon Combustion Efficiency and Sulphur Retention, Fuel, vol. 80, no.10, pp. 1405-1414 (2001).　　[Links]

Bragança, S.R., Jablonski, A., and Castellan, J. L., Quatro anos de estudo sobre o processo de dessulfuração do gás de combustão do carvão. Proceedings from the II Congresso de Engenharia de Processos do Mercosul -ENPROMER (1999).　　[Links]

Davini P., Investigation into desulphurization properties of by-products of the manufacture of white marbles of Northern Tuscany, Fuel, vol. 79, no. 11, pp. 1363-1368 (2000).　　[Links]

Hsia, C., Diffusion through $CaSO_4$ formed during the reaction of CaO with SO2 and O2, AIChE Journal, vol. 39, no. 4, pp. 688-700, April (1993).　　[Links]

Levenspiel, O. and Kunii, D., Fluidization Engineering. 2nd edition, Butterworth-Heinemann (1991).　　[Links]

Makansi, J., Few New Options Emerge for Complying with CAA Phase II, Power, vol. 137, no 7, 21-27 (1994).　　[Links]

Martin, A.E. (Ed.), Emission Control Technology for Industrial Boilers, New Jersey: Noyes Data Corporation (1981).　　[Links]

Pacheco, R.G., Um Estudo Fluidinâmico do Leito Fluidizado Rápido, master´s thesis, Federal University of Rio Grande do Sul UFRGS (1992).　　[Links]

Pettijohn, F.J., Sedimentary Rocks, p. 422. New York: Harper and Brothers (1957).　　[Links]

Renz, U., Fluidized Bed Coal Combustion. Seminar on coal technology Federal University of Santa Catarina UFSC (1981).   [Links]

Sotirchos, S.V. and Zarcanitis, S., Inaccessible Pore Volume Formation During Sulfation of Calcine Limestones, AIChE Journal, vol. 38, no, 2, 268-273 (1992).   [Links]

Slack, A. V. and Falkenberry, H.L., Sulfur-dioxide Removal from Power Plant Stack Gas by Limestone Injection, Journal of Engineering for Power, 5-10 (1970).   [Links]

Valk, M., Atmospheric Fluidized Bed Coal Combustion: Research, Development and Application. Coal Science Technology no. 22, p. 347. Amsterdam: Elsevier (1995).   [Links]

* To whom correspondence should be addressed