Residual Activity of Sorbent Particles with a Long Residence Time in a CFBC

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To characterize the sulfation capacity of limestone as a sorbent of SO_2 in a circulating fluidized-bed combustor (CFBC), long-term sulfation tests were carried out in a thermobalance. In order to cover the range of residence times expected in a large-scale combustor, the experiments lasted 24 h. The residual activity of the sorbent after the first hours of reaction indicated a conversion of ~ 0.1, depending on the particle's size and sulfation conditions. The shrinking core model described well these residual activities. An effective gas-phase diffusion coefficient was derived from plots of the measured conversion vs. time between 3 and 24 h. These diffusivities ranged between 1.7 and 4.1×10^{-9} m^2/s at 850°C and depended only on the limestone. It is argued that this simple description could be incorporated into more complex sulfation models of the first few hours of reaction and also account for the subsequent increases in conversion over longer time scales. It is also stressed that, to predict a sorbent's performance in a boiler, characterization techniques should be expanded to experimental time scales similar to those expected in large-scale CFBCs.

Introduction

Circulating fluidized-bed combustors (CFBC) are one of the main options for a clean, reliable, and cost-effective method for burning a wide variety of solid fuels. One of their main advantages is the possibility of burning fuels with a high sulfur content through the effective removal of sulfur dioxide by adding limestone. Limestone calcines in a boiler and the resultant lime, CaO, reacts with SO_2 and oxygen to produce $CaSO_4$. The reaction mechanism has been the subject of many experimental and theoretical investigations (Allen and Hayhurst, 1996). It is well known (Hartman and Coughlin, 1974) that the higher molar volume of $CaSO_4$ than those of CaO and $CaCO_3$, causes pore plugging in the external layers of the particles and prevents the full utilization of the sorbent. The concept of maximum conversion, x_{max}, of a sorbent is used in both empirical and most rigorous models. In the empirical models it is defined as an asymptotic or limiting value in plots of conversion against time (Lee and Georgakis, 1981; Zheng et al., 1982; Fee et al., 1983; Chang and Thodos, 1984; Adánez et al., 1994). In the grain model, it is related to the limiting size of the grains when they fill up the initial porosity of the calcined sorbent (Georgakis et al., 1979; Lindner and Simonsson, 1981; Efthimiadis and Sotirchos, 1993). In pore distribution models it is related to the thickness of the product layer and associated plugging of the mouth of a pore (Bhatia and Perlmutter, 1981; Christman and Edgar, 1983; Simons and Garman, 1986; Adánez et al., 1996). It is usually assumed that no conversion of the solid takes place after this limiting conversion.

The value of the maximum conversion, x_{max}, is affected by the same factors that affect the reactivity of the sorbent: particle size, calcination conditions, SO_2 concentration, limestone-type, and so on. Moreover, it is important to assess the quality of a limestone as a sorbent because the overall Ca/S molar ratio needed for a certain value of sulfur retention increases with decreasing x_{max}. For a given particle size and sulfation conditions, the value of x_{max} can be experimentally determined with experimental techniques such as thermogravimetric analysis (Fee et al., 1983; Chang and Thodos, 1984), differential reactors (Borgwardt et al., 1987; Mattison and Lyngfelt, 1998), and batch fluidized-bed reactors (Zheng et al., 1982; Dennis and Hayhurst, 1986; Adánez et al., 1994), all of which try to reproduce the environment in a boiler. The

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usual time given to such sulfation tests varies between 2 and 6 h.

In a CFBC boiler, the continuous circulation of solids through the cyclone implies a wide distribution of particle residence times in the system. While the fine particles not efficiently caught by the cyclone can only stay a few seconds in the riser, larger particles have average residence time of several hours in the main circulation loop. Mattison and Lyngfelt (1998) have recently published the residence time curves for three installations of different scales from 12 to 165 MW. Particles just over 200 μm have a typical average residence time between 10 and 20 h. These time scales are clearly much higher than those used in the preceding characterization studies on a laboratory scale.

The aim of this work was to investigate the relevance of the residual activities of a sorbent at typical time scales and particle sizes of CFBC boilers. Attention was also focused on the possibility of incorporating in a simple way the concept of this residual activity into the available sulfation reaction models in order to cover the whole range of residence times of CFBC systems.

Experimental Studies

Apparatus

The apparatus used was a thermo-gravimetric analyzer (TGA), Setaram TGC-85 type. It consists essentially of a quartz tube (15 mm ID) placed in an oven that can be operated at temperatures up to 1,000°C. The sample holder was a platinum basket (8 mm diameter, with a height of 2 mm). The temperature and the sample weight were continuously recorded in a computer. The reacting gas mixture (20 nL/h), which contained SO_2, O_2, and N_2, was controlled by specific electronic mass-flow controllers and was introduced at the top of the reaction tube. In addition, N_2 (6 nL/h) flowed through the microbalance heat to keep the electronic parts free of corrosive reactant gas.

Materials

Three different Spanish limestones have been used and their chemical composition and physical properties are compiled in Table 1. The Omyacarb limestone was used to test the effect of the main operating variables on the sorbent's behavior at long sulfation times. Five narrow particle-size intervals between 70 and 1,000 μm were investigated. During calcination, this limestone develops an internal pore structure of small mesopores with a unimodal size distribution. The limestones ''Horcallana'' and ''Sástago'' were also tested at the reference conditions to determine the effect of sorbent on the residual activity.

Table 1. Chemical and Physical Properties of the Limestones

	Limestones		
	Omyacarb	Sástago	Horcallana
Chemical composition			
$CaCO_3$	97.1	95.7	94.3
$MgCO_3$	0.2	0.9	1.0
Others	2.7	3.4	4.7
Loss on ignition (CO_2)	44.0	43.1	42.9
Porosity			
Raw sorbent	0.03	0.21	0.04
Calcined sorbent	0.56	0.66	0.56

Procedure

All sulfation tests were performed with the sorbent completely calcined. Sorbent calcination was carried out for 5 min in an atmosphere of nitrogen at the reaction temperature. This time was observed to be sufficient for complete calcination in the size ranges investigated. For each run, 10 mg of limestone were loaded in the basket, which was rapidly introduced into the hot furnace for quick heating of the sample. After complete calcination, the calcines were exposed to the simulated sulfation gas mixture consisting of the desired SO_2 level, oxygen, and nitrogen. The temperature and the weight of sample were recorded at 5–300-s intervals during the experiments. Plots of conversion vs. time were obtained from the measured weight, assuming that CaO was converted to $CaSO_4$. The samples were weighted at the end of the experiment in a different balance to check the accuracy of the TGA experiment. Good agreement was found in all cases between the overall conversion calculated from this final weight difference and the conversion from the TGA.

Long-term sulfation experiments, lasting typically 24 h, were performed at different temperatures between 800 and 900°C, with different particle sizes from 70 to 1,000 μm, and different SO_2 partial pressures between 500 vppm and 5,000 vppm. For comparison, a reference set of conditions was defined as temperature, 850°C; particle size, 100–250 μm; gas composition, 0.1 vol. % SO_2, 10 vol. % O_2, and N_2 as to balance.

Results and Discussion

An initial run was carried out with the Omyacarb limestone at the reference conditions. As can be seen in Figure 1, the main increase in conversion took place during the first

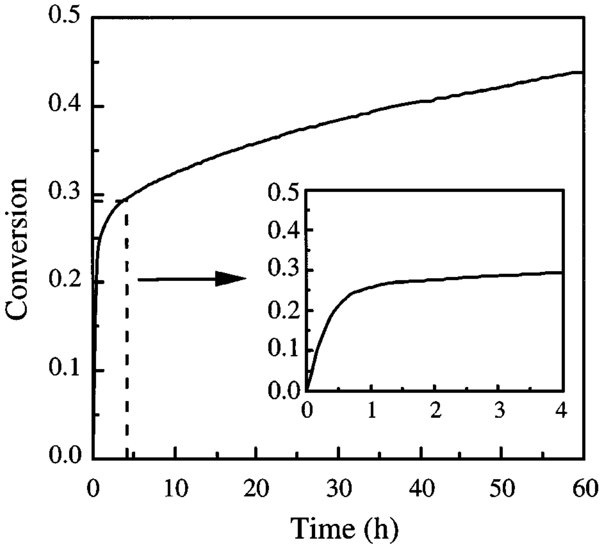

Figure 1. Sulfation conversion at long reacting time for Omyacarb limestone (850°C; 1,000 vppm SO_2; 0.1–0.25 mm).

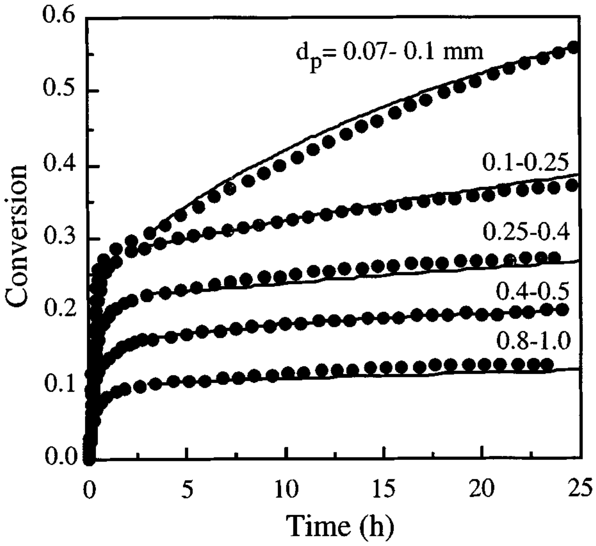

Figure 2. Particle-size effect on the sulfation conversion for Omyacarb limestone (850°C, 1,000 vppm SO_2).

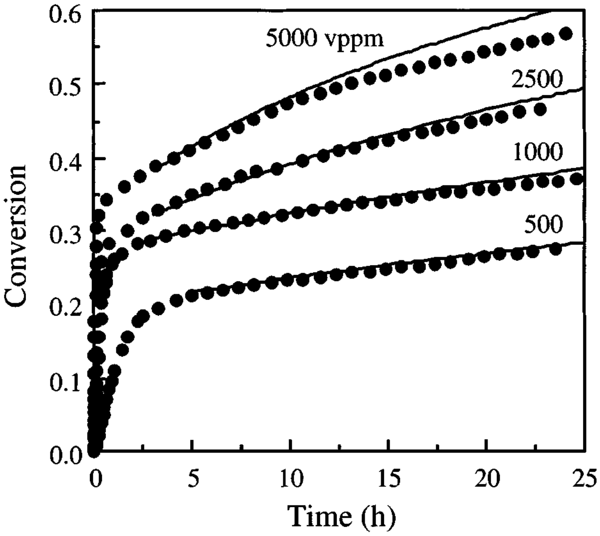

Figure 3. SO_2 concentration effect on the sulfation conversion for Omyacarb limestone (850°C; 0.1–0.25 mm).

hour and the reaction rate rapidly decreased afterwards. A reasonable value for x_{max} for this sorbent under these typical sulfation conditions would be under 0.3 (see the 0–4 h plot in Figure 1). However, the residual activity of the sorbent is evident over the 60 h time scale, with the conversion rising higher than 0.4.

Figures 2–4 summarize the results investigating the effect of particle size, temperature, and SO_2 concentration for Omyacarb limestone. They also include as solid lines the predictions of the model described below. The conversion increased with decreasing particle size and increasing SO_2 partial pressure (Figures 2 and 3). It is remarkable that for small reaction times (< 6 h), there was a maximum conversion at 850°C at the reference test conditions (Figure 4), although for a longer reaction time (> 16 h), the conversion was higher at a higher temperature (900°C). Figure 5 shows the effect of varying limestone. The residual reactivities shown by the different limestones were of the same magnitude, despite the large differences in actual conversion values.

The residual activities shown in these figures are comparable with other published results (Lee and Georgakis, 1981; Chang and Thodos, 1984) over long time scales. Also, Mattison and Lyngfelt (1998) proposed a correlation for effective reaction constants; it produces similar if not higher values than those implicit in Figures 1–5. It is, however, clear that this finding has been ignored in the past, perhaps because most of the characterization tests were developed for larger particles (~ 1 mm) used in atmospheric fluidized-bed combustors (AFBC), where the contribution of the residual activity is truly irrelevant (see Figure 2). It is also important to highlight that the experimental information contained in Figures 1–5 summarizes the main objective of this work: to show that the residual activity of the sorbents is responsible for a sorbent's conversion being higher than expected from typical sorbent characterization tests. This can have important implications when assessing the quality of a limestone as a sulfur sorbent.

A simple approach to model the observed residual activities of the sorbents was attempted. The asymptotic trends observed in the experimental results lead to the definition of two characteristic values of conversion. First, a threshold value of conversion, x_0, is defined, from which a large resistance to the sulfation reaction is present due to the formation of an external layer rich in $CaSO_4$. This varies between 1 and 3 h in our experiments, depending on sorbent and operating conditions. For practical reasons, however, a common starting point of 3 h valid for all the experiments was selected. The prediction of the sorbent conversion from 0 to x_0 is beyond the scope of this work. Appropriate empirical or

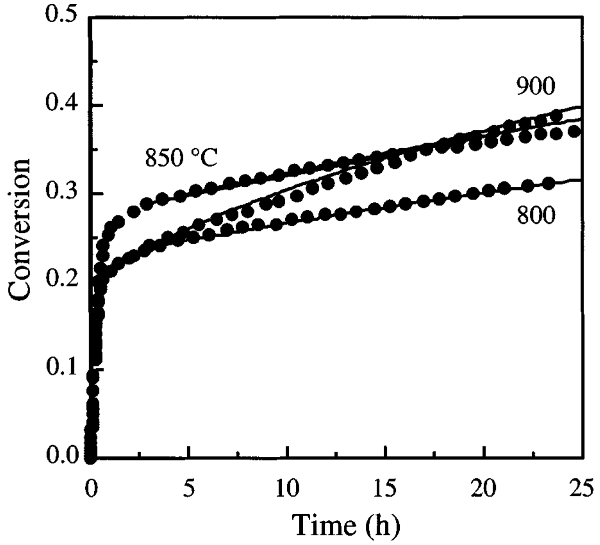

Figure 4. Temperature effect on the sulfation conversion for Omyacarb limestone (1,000 vppm SO_2; 0.1–0.25 mm).

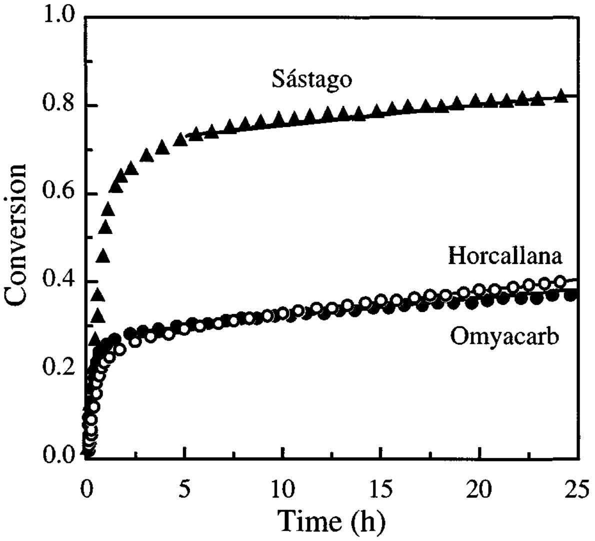

Figure 5. Type of limestone effect on the residual activity (850°C; 1,000 vppm SO_2; 0.1–0.25 mm).

mechanistic models have been published for this purpose, as mentioned in the Introduction.

The second definition is x_{lim}, as the limit sulfation conversion of the sorbent when all the initial porosity developed during calcination is filled with $CaSO_4$. It is assumed that the sorbent evolves toward x_{lim} in all the conversion curves of Figures 1–5. The value of x_{lim} depends on the initial porosity of the sorbent and on the molar volume ratio of product to reactant, Z_s. Assuming no changes in particle size and no impurities, we have

$$x_{\mathrm{lim}} = \frac{\epsilon_{\mathrm{CaO}}}{(Z_s - 1)(1 - \epsilon_{\mathrm{CaO}})}. \tag{1}$$

A molar volume ratio from $CaSO_4$ to CaO of 2.72 was used, as suggested by Sotirchos and Zarkanitis (1992). The porosity of the calcined Omyacarb limestone is 0.56 and leads to a theoretical maximum conversion of 0.74. Sorbents with high initial porosity like Sástago limestone could yield fully converted particles with x_{lim} almost equal to 1. Anthony et al. (1998) have recently demonstrated in their sulfation experiments with ashes from industrial-scale FBC boilers, that sulfation goes to completion over periods of time of up to 105 days. These time scales are two orders of magnitude higher than those considered in this work, and therefore it is considered that the final conversion of the large particles leaving a CFBC will be between x_0 and x_{lim}.

In this work, the increase in conversion due to the residual activity of the sorbent was described with the shrinking-core model (SCM). The equation for the conversion varying with time in the SCM (Levenspiel, 1972) was rewritten to include the theoretical maximum conversion, x_{lim}:

$$\frac{t}{\tau} = 1 - 3\left(1 - \frac{x}{x_{\mathrm{lim}}}\right)^{2/3} + 2\left(1 - \frac{x}{x_{\mathrm{lim}}}\right), \tag{2}$$

where the time needed to reach limiting conversion is

$$\tau = \frac{\rho_{\mathrm{Ca}} x_{\mathrm{lim}} d_p^2}{24 D_e C_{\mathrm{SO}_2}} \tag{3}$$

Equation 2 can be rewritten for the part of the curve after x_0:

$$\frac{t - t_0}{\tau} = 3\left[\left(1 - \frac{x_0}{x_{\mathrm{lim}}}\right)^{2/3} - \left(1 - \frac{x}{x_{\mathrm{lim}}}\right)^{2/3}\right] - 2\left(\frac{x - x_0}{x_{\mathrm{lim}}}\right), \tag{4}$$

where t_0 is the time to reach x_0. With this definition, the subsequent gains in conversion $(x - x_0)$ after 3 h were compared with the values of $(x - x_0)$ predicted by Eq. 4. Fitting the experimental data available at the different gas concentration and particle sizes shown in Figures 2–3 and using Eqs. 3 and 4, a single value of D_e of 1.7×10^{-9} m²/s was obtained at 850°C for Omyacarb limestone. To include measurements at different temperatures, it was assumed that

$$D_e = 0.00016 \exp(-107\ (\mathrm{kJ/mol})/RT). \tag{5}$$

Finally, new values of D_e were obtained at 850°C for the other limestones: 2.4×10^{-9} m²/s for the Horcallana and 4.1×10^{-9} m²/s for the Sástago limestone.

The experimental and predicted increases in conversion are compared in Figure 6, when using Eq. 5 for the effective diffusion coefficient; Figures 2–5 also include as solid lines the predicted values of conversions. The most important relative deviations were in the larger and smaller particle-size ranges. However, taking into account the range of experimental conditions used, the quality of the fit is satisfactory.

In the shrinking-core model the conversions are associated with the thickness of the product layer as

$$e = \frac{d_p}{2}\left[1 - \left(1 - \frac{x}{x_{\mathrm{lim}}}\right)^{1/3}\right]. \tag{6}$$

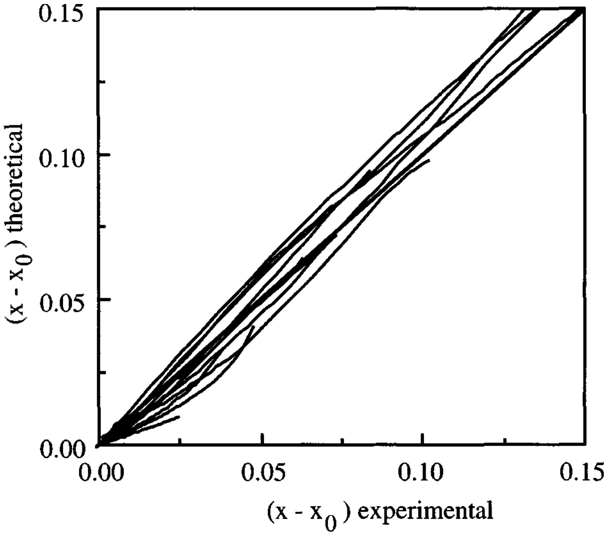

Figure 6. Experimental vs. predicted curves of all the experiments.

It is remarkable that in the interval of particle sizes used for the Omyacarb limestones, e ranged between 12 and 20 μm. SEM analysis of selected samples confirmed that this sorbent develops a strong core/shell structure and that these are reasonable values for this parameter.

The presence of an external product layer in the particles and the high activation energy obtained in this work (107 ± 4 kJ/mol) seems to indicate that a solid diffusion mechanism could be responsible for the residual activity observed in the samples. Borgwardt et al. (1987) proposed that the migrating species in the solid $CaSO_4$ layer were $O^=$ and $SO_4^=$ with $CaSO_4$ forming at the $CaO/CaSO_4$ interface. However, Hsia et al. (1993) demonstrated that the diffusion of Ca^{++} and $O^=$ ions through the product layer is taking place, with the sulfation reaction progressing at the $CaSO_4$/gas interface. In both cases, high activation energies were reported for these solid-state ionic diffusion mechanism. On the other hand, Christman and Edgar (1983) reviewed the wide range of values (6×10^{-13}–3×10^{-10} m^2/s) reported by various workers for the effective diffusivity of SO_2 through $CaSO_4$ at 850°C. The values of D_e (around 10^{-9} m^2/s) obtained with the limestones used in this work were much higher than any of the previously reported values for the product layer diffusivity, D_s. Therefore, it is difficult to accept a solid diffusion mechanism as the unique mechanism responsible for the residual activities measured in this work.

Hartman and Coughlin (1976) and Kocaefe (1986) introduced the concept of residual porosity in the product layer in their particle-reaction models. This residual porosity would be beyond the detection limits of available equipment, but is a reasonable assumption ascribed to local nonuniformities in the $CaSO_4$ product layer (Hartman and Coughlin, 1976). It also seems possible in our case that the tortuous morphology in the highly converted external layers of the particle can justify very small values of residual porosity. This would allow a slow mechanism of gas diffusion toward the unreacted core of the particle. However, with such a mechanism the activation energy should be much lower. This apparent contradiction between gas and solid diffusivity mechanism in our data should be considered in future particle models covering the whole range of sulfation conversions, but they are clearly beyond the scope of this work. Although our analysis of residual activities is approximated, the fitted value of D_e from the SCM is good enough to describe the conversion over long time scales for the sizes of practical interest.

The values obtained for D_e are independent of the value of x_0 considered for a given limestone. This allows the application of Eq. 4 after the threshold value of x_0 without attending to the reaction story of the particle before that value. In addition, the order of magnitude of the values for the different sorbents was similar despite the large differences in x_0. To analyze the sensitivity of the predictions, Figure 7 simulates the effect of D_e on conversion increments under comparable conditions. The figure has been constructed using a 15-micron thickness of product layer for all the particle sizes to define x_0 and allowing 10 h of reaction time. As can be seen in this figure, the particle-size ranges over 0.4 mm, typical of bubbling fluidized-bed combustors, are practically insensitive to D_e and show low residual activities and conversion improvements. The results for the finer particle material (< 70 μm) are irrelevant because they cannot stay for so long in the boiler and because the SCM is not a good representation of the sulfation process in these size ranges. The particle-size ranges between 70 and 400 μm are very sensitive to the value of D_e, however, and present relevant conversion improvements in a time scale adequate for CFBC reaction conditions.

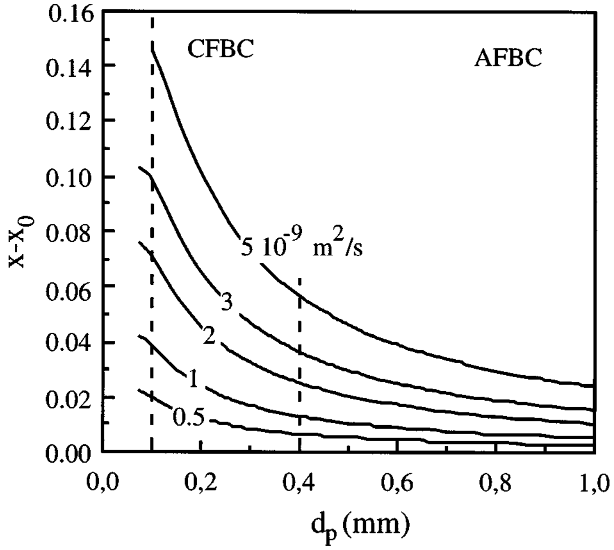

Figure 7. Particle size effect on the residual activity of the sorbent for different effective diffusion coefficients.

In view of the previous discussion it seems necessary to review the way limestones are assessed as potential sorbents for a CFBC. In order to better estimate the sulfation capacity of a sorbent, long-lasting sulfation experiments are needed in the characterization tests for the particle-size ranges sensitive to reasonable values of D_e. Sorbents showing large values of x_0 are still preferred over those with low values, but a better picture of the quality of the sorbent is obtained if the values of conversion are experimentally obtained at typical time scales of the sorbent in the boiler.

Finally, the results presented here can also help explain why some large-scale boiler have performed better than expected from the point of view of sulfur retention. Mattison and Lyngfelt (1998) reported values of sorbent conversion in large-scale boilers higher than those obtained from characterization tests. They review some explanations for these disagreements based on attrition mechanisms and alternating oxidizing/reducing conditions in the different zones in the boiler. The residual activities reported in this work might not by themselves be enough to explain the differences observed in these cases, but could strongly reduce the gap between predicted and observed sorbent conversions in large-scale units.

Conclusions

The sulfation reaction of limestone particles in the typical time scales and reaction conditions in a CFBC boiler shows a residual activity that produces relevant changes in conversion for the particle-size ranges between 0.07 and 0.4 mm.

The SCM can adequately interpret the measured residual activities using a characteristic effective gas-diffusion coefficient dependent only on the sorbent. This coefficient ranges between 1.7×10^{-9} and 4.1×10^{-9} m^2/s at 850°C for the three limestones studied in this work. The SCM can be easily incorporated into available particle sulfation reaction models to account for the subsequent increase in conversion after the first few hours of reaction.

The sulfation capacity of a limestone and its potential quality as SO_2 sorbent in a CFBC boiler is better assessed if long-lasting tests of sulfation are conducted during laboratory characterization tests. The results from these tests can reduce some reported disagreements between the sorbent conversion reached in large-scale units and those obtained in short-duration characterization tests.

Acknowledgments

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Notation

C_{SO_2} = SO_2 concentration in the bulk gas, mol/m^3
D_e = effective gas diffusivity of SO_2, m^2/s
d_p = particle diameter, m
R = ideal gas constant, 8.314 J/mol·K
T = temperature, K
x = calcium conversion during sulfation
ρ_{Ca} = molar density of Ca in the particles, mol/m^3

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