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SULFATION RATES OF CYCLED CaO PARTICLES IN THE CARBONATOR OF A Ca-LOOPING CYCLE FOR POST-COMBUSTION CO₂ CAPTURE

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Abstract

Calcium looping is an energy-efficient CO₂ capture technology that uses CaO as a regenerable sorbent. One of the advantages of Ca looping compared with other post-combustion technologies is the possibility of operating with flue gases that have a high SO₂ content. However, experimental information on sulfation reaction rates of cycled particles in the conditions typical of a carbonator reactor is scarce. This work aims to define a semi-empirical sulfation reaction model at particle level suitable for such reaction conditions. The pore blocking mechanism typically observed during the sulfation reaction of fresh calcined limestones is not observed in the case of highly cycled sorbents ($N > 20$) and the low values of sulfation conversion characteristic of the sorbent in the Ca-looping system. The random pore model is able to predict reasonably well the CaO conversion to CaSO₄ taking into account the evolution of the pore structure during the calcination/carbonation cycles. The intrinsic reaction parameters derived for chemical and diffusion controlled regimes are in agreement with those found in the literature for sulfation in other systems.

Introduction

Post-combustion CO₂ capture using CaO as a regenerable solid sorbent (or calcium looping, CaL) is a rapidly developing technology because of its potential to achieve a substantial reduction in capture cost and because of the energy penalties associated with more mature CO₂ capture systems^{1,2}. In a post-combustion CaL system, CO₂ from the combustion flue gas of a power plant is captured by using CaO as sorbent in a circulating fluidized bed (CFB) carbonator operating between 600-700 °C. The stream of partially carbonated solids leaving the carbonator is directed to the CFB calciner, where the solids are calcined, thereby regenerating the sorbent (CaO) and releasing the CO₂ captured in the carbonator. In order to calcine the CaCO₃ formed in the carbonator and to produce a highly concentrated stream of CO₂, coal is burned under oxy-fuel conditions at temperatures above 900 °C in the calciner. One of the main distinctive characteristics of this process is its lower energy penalty, as operation at high temperatures allows for efficient heat integration of the full system in the power plant^{3,4,5,6,7,8}.

Another known benefit of CaL systems compared with other post-combustion technologies, such as amines, is the theoretical capability of operating with flue gases that have a high SO₂ content. This is because the calcined limestones present in carbonator and calciner reactors are known to be excellent desulfurization agents, and they are routinely used in many commercial scale power plants, including circulating fluidized bed combustors (see review by 9). Although several recent works have investigated sulfation phenomena in CaL systems^{10,11,12,13,14,15,16,17}, there is very little quantitative information on the sulfation rates of CaO in the carbonator and calciner reactor environments.

An important difference between sulfation studies with CFB combustors and sulfation studies with CaL systems concerns the typical range of conversion to CaSO_4 that can be expected of each of these systems. An obvious design target of any commercial flue gas desulfurization process is to make the most use of the Ca and to achieve maximum conversion to CaSO_4 . However, in a CaL system, there is generally a need for a large make up flow of low cost limestone to compensate for the decay in the sorbent's CO_2 carrying capacity along cycling. A mass balance for the recycling of Ca solids has shown¹⁸ that this leads to CaSO_4 contents well below 5mol% in a CaL system, even when high sulfur content fuels are used. This has important implications for the debate of the effect of sulfur on CaL systems, because this low conversion of the Ca sorbent to CaSO_4 is well below the limit of conversion required to achieve the extensive pore plugging that is characteristic of highly sulfated particles (see review by Anthony⁹). The purpose of this work therefore is to examine more fully the sulfation phenomena associated with these low levels of conversion to CaSO_4 .

Several models have been proposed for studying and describing heterogeneous sulfation reactions and pore plugging processes under different reaction controlled regimes and for different sorbents^{19,20,21,22,23,24,25}. The models increase in complexity when they need to quantify the diffusion phenomena of the reactants passing through plugged pores. However, there is a general consensus concerning what happens in the initial stages of the reaction (low sulfation conversions). The first quantitative descriptions of the rate of reaction of SO_2 with CaO ^{26,27} established that, in the absence of diffusion through the pores of the particles, the reactivity of the sorbent towards SO_2 increases with the internal surface area. The overall reaction rate in these conditions is controlled by the chemical reaction at low values of sulfate conversion and by

gas diffusion through a layer of CaSO_4 formed over the CaO sorbent that increases as the sulfation conversion increases. Regarding the effect of SO_2 concentration in gas phase, there is general agreement the the reaction order ranges from 0.6 to 1^{28,20,22,29}. This background information should be valuable in modelling the sulfation rates of CaO particles in the typical conditions of CaL systems.

Another important difference between early works on the sulfation reaction of CaO in combustion environments and the present study is to do with the range of temperatures. The most suitable mathematical models for describing the rate of sulfation of individual particles are usually fitted to the data obtained at temperatures characteristic of CFBC (around 850 °C). However, these conditions differ considerably from those of a carbonator reactor working with a flue gas at lower temperatures (650 °C).

Finally, it is necessary to take into account the special characteristics of the CaO particles cycling in a CaL capture system, where the reversible carbonation reaction of CO_2 with CaO has a strong impact on the textural properties of the material. It is well known that the CO_2 carrying capacity of CaO sorbents decays with number of calcinations/carbonations^{30,31} due to a sintering mechanism that drastically reduces the surface with the increasing number of cycles. In a scenario where SO_2 is present in the flue gas entering the carbonator reactor, there is additional deactivation of the CaO sorbent due to the formation of CaSO_4 . Several works have shown^{11,12,13,17} that SO_2 accelerates the decrease in CO_2 carrying capacity of a sorbent during cycling even when a low ratio of SO_2/CO_2 is used. One important conclusion of these cyclic tests is that the performance of limestones may differ considerably during sulfation in contrast to their similar

behaviour during carbonation¹³. In their studies of the performance of calcium aluminate pellets during co-capture tests of CO₂ and SO₂ Manovic et al. showed that the deactivation of synthetic sorbents (calcium aluminate pellets) is greater than that of natural limestone sorbent due to their higher reactivity towards SO₂¹⁷.

On the other hand, the sintering process of CaO under cyclic carbonation calcination cycles can have a positive impact on sorbent utilization during sulfation. Some researchers have found that the sulfation behaviour of CaO is enhanced (higher maximum sulfation conversions are achieved) during the calcination/carbonation cycles^{10,13,14}. This is because the sintering of the particles during carbonation-calcination is accompanied by a widening of the pores to diameters of several 100s nm after extended (100) cycles³². The opened structures formed during the calcination/carbonation cycles are then able to accommodate the bulky product layer of CaSO₄, thus reducing the pore blocking mechanism which limits CaO conversion during sulfation. On the basis of this sorbent behaviour, some researchers have suggested the idea of using the spent sorbent from carbonate looping as feedstock material for SO₂ retention in CFB boilers during coal combustion^{13,15,16}. This may be one of the reasons why most of the published data on the sulfation of spent sorbents is related with high temperatures typical of combustion temperatures (850-900 °C) and there is lack of experimental information on sulfation rates under carbonation temperatures (650°C).

The focus in this work is on the capture of SO₂ from the flue gas fed into the carbonator reactor, as this operates in conditions that may need to reconsider and reformulate the application of existing models at particle level to describe the sulfation reaction rates of CaO. Indeed, despite

the large body of literature on the reaction of CaO with SO₂ in a wide range of conditions relevant to the operation of CFBCs, there is insufficient experimental information on sulfation reaction rates in the conditions characteristic of a carbonator reactor (i.e. particles that have undergone very different numbers of carbonation-calcination cycles, having substantially different textural properties and with expected conversions to CaSO₄ compared to that of CFBC systems). This work addresses this knowledge gap and presents what we believe to be the first results of an investigation to define a semi-empirical sulfation reaction model at particle level suitable for the conditions characteristic of a carbonator reactor in a Ca-looping postcombustion system.

EXPERIMENTAL

Three different limestones with particle sizes in the range of 63-100 µm were used for this study. Their chemical composition is shown in Table 1. The calcination/carbonation cycling and the sulfation of the sorbents was experimentally studied using a TGA analyzer especially designed for carrying out long calcination-carbonation cycles, as described elsewhere³³. This TG consists of a quartz tube installed in a two-zone furnace which is able to work at two different temperatures. The furnace can be moved up or down by means of a pneumatic piston and its position with respect to the sample allows a rapid change from calcination (950 °C) to carbonation temperatures (650 °C) and viceversa. The system is equipped with a microbalance that continuously measures the weight of the sample which is held in a platinum basket. The gas mixture (air/CO₂/SO₂) was prepared using mass flow controllers and was fed into the bottom of the quartz tube. The weight and temperature of the sample were continuously recorded on a computer.

The experimental procedure starts with the calcination carbonation cycling of the limestone for a certain number of cycles. During these tests, calcination was carried out in air at 950 °C and carbonation under 10% CO₂ in air at 650 °C. After cycling, the sample temperature was allowed to stabilize for 10 minutes until a temperature of 650 °C was reached. A mixture of SO₂ with air was then introduced into the quartz tube in order to begin sulfation. Tests were carried out to establish the experimental conditions (sample mass and total gas flow) needed to avoid external diffusion effects. In the light of the results, the total volumetric flux was finally set to 2.25×10^{-5} m³/s, (corresponding to 0.05 m/s at 650 °C). It was also established that a sample mass below 3 mg was necessary to eliminate external mass diffusion effects (i.e. at T=650 °C and 500 ppmv of SO₂). CaO conversion of the sorbent was calculated from the weight gain assuming that CaSO₄ would be the main product of the reaction between CaO and SO₂ under the experimental conditions of this work. After the end of each run, the samples were weighed using a different balance to check the accuracy of the TGA. A good agreement between both series of measurements was obtained in all cases.

Table 1. Chemical composition (% wt) of limestones used in this work.

RESULTS AND DISCUSSION

Figure 1a shows the evolution of CaO conversion to CaSO₄ with time for limestones tested after a first calcination at a temperature of 650 °C using 500 ppmv of SO₂. As can be seen, the three sorbents exhibit an initial fast period followed by a second period with a lower reaction rate during which the X_{CaSO_4} tends to stabilize to an almost constant value. In the case of the

Compostilla and Imeco limestones, the sulfation rate of CaO fell sharply after ten minutes of reaction, to a X_{CaSO_4} of 0.16 and 0.19 respectively. The reactivity of the Enguera limestone towards sulfation was much higher, yielding a X_{CaSO_4} of 0.35 at the end of the sulfation period. The drastic slowing down of the sulfation process has been reported widely in the literature and is attributed to pore blockage due to the different molar volumes of CaO and CaSO_4 (16.9 and $46.0 \text{ cm}^3/\text{g}$ respectively)⁹.

Figure 1b shows the CaO conversions to CaSO_4 after 50 calcination/carbonation cycles. As can be seen, the evolution of X_{CaSO_4} is quite similar for the three sorbents after cycling, despite the different behaviours of the freshly calcined limestones (Figure 1a). This is a clear indication of the strong effect of a large number carbonation-calcination cycles on the pore structure of CaO particles, irrespective of their origin, as revealed in previous studies on carbonation³⁴.

Figure 1. X_{CaSO_4} vs time for limestones used in this work after the first calcination (a) and 50 calcination/carbonation cycles (b) ($T=650 \text{ }^\circ\text{C}$, SO_2 concentration=500ppmv).

Certain similarities between Figure 1a and 1b are worth highlighting. On the one hand, the sulfation of the CaO cycled particles seems to maintain a certain transition (at about 300s in these figures) between two stages in the rate of reaction. The fast reaction stage has a less inclined slope compared to the equivalent period in the fresh sorbent (Figure 1a), and this can be attributed to the smaller surface area of the CaO particles after 50 carbonation-calcination cycles. Furthermore, the reduction in the reaction rate during the second stage is less pronounced in the case of the cycled sorbents (as the solid lines show). Even more interesting is the fact that in

Figure 1b the reaction rate remains almost constant until the very end of the sulfation experiment, in contrast with what one would expect when the pore blockage mechanism is takes place (as in Figure 1a). This behaviour might be expected in view of the evolution of the sorbent surface, with cycling, towards one with a more opened texture and wider pores^{13,17,32,35}. A comparison of the experimental data in Figure 1a and 1b shows the importance of taking into account the evolution of sorbent texture during the calcination/carbonation cycles when modeling the sulfation process and determining the rate constants, as will be discussed later on.

Experiments with different particle sizes were carried out to evaluate radial diffusion resistances throughout the pore network of the particles, focusing on the low level of sulfate conversion (fast reaction regions in Figure 1). Figure 2 shows the CaO conversion to CaSO₄ for the freshly calcined and cycled (N=20) Compostilla limestone of two particle sizes, 63-100 and 400-600 µm respectively. As can be seen, the reaction rates are similar for both sizes. This indicates that the SO₂ concentration is constant throughout the particle and that the sulfation rate can be described by means of a homogeneous model for these particle size ranges, common in Calcium looping applications with CFB technology. However, this approach should always be reconsidered when using particles of a larger size in other systems.

To study the effect of SO₂ on the sulfation rate of CaO, tests with different concentrations were carried out at a temperature of 650 °C. The effect of the SO₂ concentration on X_{CaSO₄} in the case Compostilla limestone after the first calcination cycle is shown in Figure 3, where the SO₂ concentration ranges from 500 to 3000 ppmv. As can be seen, the SO₂ concentration has a

marked effect on the slope of the initial stage of the sulfation process and on the final conversion of the sorbent after 20 minutes of reaction.

Figure 2. Effect of the particle size on the sulfation of CaO after the first calcination (empty symbols) and 20 calcination/carbonation cycles (filled symbols) ($T=650\text{ }^{\circ}\text{C}$, SO_2 concentration=500ppmv).

As already mentioned, different reaction orders can be found in the literature depending on the sulfation conditions. To determine the reaction order under the sulfation conditions tested in this work, the maximum sulfation rate ($\Delta X/\Delta t$) for the initial period (up to reaction times of 100 s) was represented against the SO_2 concentration. Figure 3b shows the results obtained for the slopes of the curves in the case of the fresh calcined Compostilla limestone. As can be seen, a good linearity is observed indicating a pseudo-first order reaction respect to SO_2 . Figure 2 shows the results obtained for the other limestones ($N=1$) and for the Compostilla limestone after 20 calcination/carbonation cycles confirming the first reaction order.

Figure 3. Effect of SO_2 concentration on X_{CaSO_4} for the fresh calcined Compostilla limestone ($N=1$) ($T=650\text{ }^{\circ}\text{C}$) (a) and the maximum reaction rate vs SO_2 concentration (b).

The experimental results presented above were interpreted in this work using the random pore model (RPM) proposed by Bhatia³⁶ and recently adapted to the carbonation reaction in CaL systems^{37, 38}. This model has also been previously applied to freshly calcined limestones to study the diffusion and kinetic resistances involved in the sulfation process²⁰. The RPM model has a

general expression which is valid for solid-gas reactions and which is also applicable to porous systems with product layer resistance. Thus:

$$\frac{dX}{dt} = \frac{k_s S C \sqrt{1 - \psi \ln(1 - X)}}{(1 - \varepsilon) \left[1 + \frac{\beta Z}{\psi} (\sqrt{1 - \psi \ln(1 - X)} - 1) \right]} \quad (1)$$

where:

$$\beta = \frac{2 k_s a \rho (1 - \varepsilon)}{b M_{CaO} D} \quad (2)$$

and k_s is the rate constant for the surface reaction, S is the reaction surface area per unit of volume, ε is the porosity of the particles, D is the effective product layer diffusivity and C is the SO_2 concentration. In Eq. 2, Ψ is a structural parameter that takes into account the internal particle pore structure which can be calculated as:

$$\psi = \frac{4 \pi L (1 - \varepsilon)}{S^2} \quad (3)$$

where L is the initial pore length in the porous system per unit of volume, S is the initial surface area per unit of volume and ε is the porosity. For a chemically controlled reaction, the general rate expression from Eq. 1 can be simplified and integrated to yield the following equation [36]:

$$\frac{1}{\psi} [\sqrt{1 - \psi \ln(1 - X)} - 1] = \frac{k_s S C t}{2(1 - \varepsilon)} \quad (4)$$

On the other hand, when chemical kinetics and diffusion through the product layer are controlling the overall reaction rate, Eq. 1 can be integrated to the following equation:

$$\frac{1}{\psi} [\sqrt{1 - \psi \ln(1 - X)} - 1] = \frac{S}{(1 - \varepsilon)} \sqrt{\frac{D M_{CaO} C t}{2 \rho_{CaO} Z}} \quad (5)$$

Textural parameters used as inputs in the RPM model (S , L and ε) can be determined from experimental measurements²⁰. In the case of cycled CaO , since the textural properties (S_N , L_N)

change during cycling, their values for each cycle need to be known before the model can be applied. To avoid the need for experimental measurement of these parameters and in the absence of a detailed sintering model able to estimate the pore size distribution during cycling, we adopted a similar methodology to that proposed by Grasa et al.³⁷ applying the random pore model to the carbonation reaction of the cycled particles. Assuming that CaCO_3 forms a fairly constant layer at the end of the fast carbonation period³² and the total pore volume remains constant with the number of cycles, these authors proposed to determine S_N and L_N for each cycle, from the initial values (S_0 and L_0) and the maximum CO_2 carrying capacity of the sorbent (X_N) as follows:

$$S_N = S_0 X_N \quad (6)$$

$$L_N = L_0 X_N \frac{rp_0}{rp_N} \quad (7)$$

where S_0 and L_0 are the values corresponding to the initial fresh calcined limestones, and rp is the pore radius (rp_0 initial value, rp_N after N cycles). The maximum carrying capacity (X_N) in each cycle can be calculated using the following equation proposed by Grasa et al.³⁹:

$$X_N = \left(\frac{1}{\frac{1}{(1 - X_r)} + k N} + X_r \right) \quad (8)$$

where k is the deactivation constant, X_r is the residual conversion after an infinite number of cycles and N is the number of cycles. Values of $k=0.52$ and $X_r=0.075$ have been proven to be valid for a wide range of sorbents and carbonation conditions and have been used in this work. The values calculated for X_N by means Eq. 8 were compared with the experimental CO_2 carrying capacities obtained during TGA cycling and a good agreement was found. We estimated the initial surface (S_0) area of the fresh calcined limestones from the maximum CO_2 carrying

capacity of the sorbent in the first cycle assuming the CaCO_3 layer thickness at the end of the fast reaction regimen to be 49 nm^{32} . This yields an initial value of $30 \cdot 10^6 \text{ m}^2/\text{m}^3$ assuming an initial CO_2 carrying capacity of 0.7 (using $N=1$ in Eq. 8). The initial values of pore length (L_0) and porosity (ϵ) used for the three limestones were $4.16 \cdot 10^{14} \text{ m}/\text{m}^3$ and 0.46, respectively. These values were taken from a study of Grasa et al.³⁷ in which calcined Imeco limestone was characterized by mercury porosimetry.

Once the evolution of the surface area (S_N) and Ψ_N were calculated with the number of cycles, the reaction parameters, k_s and D , were determined by fitting Eqs. 4 and 5 to the experimental data. Figure 4 shows an example of the fitting of these equations to the experimental data obtained during the sulfation of Enguera limestone after 20 cycles of calcination/carbonation. Figures 4a and 4b represent the left hand side of Eqs. 4 and 5 against time and time^{1/2}, respectively. From the slopes of the straight lines, k_s and D can be calculated. As can be seen from these figures, there is a clear threshold between the chemical and the diffusion controlled regime that can be easily identified for $f(\Psi) \sim 0.5$ which corresponds approximately to $X_{\text{CaSO}_4} = 0.10$. A similar marked threshold was observed for the other samples studied. This indicates that under these experimental conditions and with this particle size, the overall reaction rate is initially controlled by the chemical reaction rate that takes place over the entire surface of the sorbent. However, as the reaction proceeds, the surface is covered by a layer of CaSO_4 and diffusion through the product layer becomes the limiting step. No pore diffusion effects were detected in the experiments or used in the model.

Figure 4. Fitting of Eq. 4 (a) and 5 (b) to the experimental data obtained for the Enguera limestone at N=20 (T=650 °C, SO₂ concentration=500 ppmv).

Before discussing the values of k_s and D (shown in Table 2), it may be useful to test the suitability of this model for describing the evolution of X_{CaSO_4} with time. CaO conversion to CaSO₄ with reaction time can be calculated using the following equations which can be derived from Eqs. 4-5:

a) for the chemically controlled regime:

$$X = 1 - \exp\left(\frac{1 - \left(\frac{\tau}{2}\psi_N + 1\right)^2}{\psi_N}\right) \quad (9)$$

b) for the diffusion controlled regime:

$$X = 1 - \exp\left(\frac{1}{\psi_N} - \frac{\left[\sqrt{1 + \beta Z \tau} - \left(1 - \frac{\beta Z}{\psi_N}\right)\right]^2 \psi_N}{(\beta Z)^2}\right) \quad (10)$$

where

$$\tau = \frac{k_s C S_N t}{(1 - \varepsilon)} \quad (11)$$

Figure 5 compares the experimental values with those calculated for Compostilla limestone for different numbers of cycles. In this figure, the transition between chemically and diffusion controlled regime has been obtained from the experimental results (typically around 120-180 s). Moreover, X_{CaSO_4} has been calculated using the k_s and D values derived for each cycle. As can be seen in the figure, the model only predicts satisfactorily the CaO conversion up to a value of ~

0.10 in the case of the fresh calcined limestone ($N=1$), which corresponds to a reaction time of around 4 minutes. From this point, the calculated values clearly overpredict the experimental ones. In contrast, for the sorbent obtained after 10 calcination/carbonation cycles, the model is able to calculate the sorbent conversion up to values of $X_{\text{CaSO}_4} = 0.2$ which corresponds to a reaction time of approximately 10 minutes. In the case of the sorbent that has been cycled 20 and 50 times, the X_{CaSO_4} values calculated with the RPM model are in close agreement with the experimental ones over the entire reaction period.

The fact that the model correctly predicts the evolution of the sulfation conversion of the sorbent obtained after many carbonation-calcination cycles is a strong validation of the RPM model when applied to our results. It shows that the product layer of CaSO_4 is able to grow around the whole particle without experiencing any geometrical restrictions. The homogeneous model is not valid for particles derived from fresh calcined limestone because they undergo pore plugging as reaction proceeds. In the case of $N=10$, the pore structure must be in an intermediate stage.

Figure 5. Comparison of experimental and calculated values of X_{CaSO_4} for Compostilla limestone with different numbers of cycles ((a) first cycle, (b) higher cycles) ($T=650\text{ }^\circ\text{C}$, SO_2 concentration=500 ppmv) (calculated values-solid lines).

In a postcombustion Ca-looping system, most particles will have been cycling the system 10s of times depending on the make up flow ratio of fresh limestone³⁴. Therefore, the assumption that the sulfation reaction progresses homogeneously in the particles, as indicated by equations 1-8, will serve as an adequate approximation for practical reactor modelling purposes. A good

agreement between the calculated values for cycled particles was found for each limestone, indicating the intrinsic nature of the values of k_s and D . In contrast, the best-fit values for the first cycle were clearly lower than the average values for all three limestones, especially in the case of the effective product layer diffusivity (D), which tends to be one order of magnitude lower. This can be explained by taking into account that the reaction surface in the particles has been calculated by means of Eqs. 6 and 8, which will tend to overestimate the reacting surface when small pores (that are prompt to CaSO_4 plugging) are present. The average values of k_s and D for each limestone are summarized in Table 2. These have been calculated using the values of k_s and D calculated for each cycle, except those corresponding to the fresh calcined limestone ($N=1$).

Table 2. Calculated kinetic rate parameters (k_s and D) for the different limestones at 650°C.

The values presented in Table 2 are in agreement with those found by Bhatia²⁰ for fresh calcined sorbents at temperatures of around 650 °C. Table 2 also shows the sulphate conversion at which the transition between the chemical and diffusion controlled regime is experimentally observed. From the values of X_{CaSO_4} and the surface area (S_N), it is possible to estimate the thickness of the product layer (h) at which the reaction becomes diffusion controlled by means of the following equation:

$$h = \frac{X_{\text{CaSO}_4} \rho_{\text{CaO}} V_{\text{MCaSO}_4}}{S_N M_{\text{CaO}}} \quad (14)$$

The calculated values of h are shown in Table 2. An average CaSO_4 layer thickness of 8.5 nm is obtained. This average value can be used to estimate the sulphate conversion that marks the transition between the kinetic and the diffusion controlled regimes.

Although this work focussed on the carbonator reactor, where the operation temperature will be fairly constant at around 650 °C, we attempted to determine the influence of the temperature on the kinetic rate parameters by means of the Arrhenius equation:

$$k_s = k_{s0} \exp(-E_{ak} / RT) \quad (15)$$

$$D = D_0 \exp(-E_{aD} / RT) \quad (16)$$

For this purpose, we carried out tests at higher temperatures to determine k_s and D . However, diffusional resistances were observed during the tests at higher temperatures, which could not be avoided in our experimental set-up. To overcome this problem and to reduce the number of adjustable parameters, we determined the values of the pre-exponential factors, assuming an activation energy of 56 kJ/mol and 120 kJ/mol as calculated by Bhatia²⁰ for k_s and D , respectively. The results obtained are shown in Table 3.

Table 3. Kinetic parameters of Eqs. 15 and 16 for the three limestones.

Figure 6 shows the experimental evolution of X_{CaSO_4} with sulfation time together with those calculated using the average values of Table 2 and assuming a layer thickness of 8.5 nm for Enguera and Compostilla limestone with different numbers of cycles. As can be seen, there is reasonable agreement between the experimental and calculated values, confirming the suitability of the model for determining the sulfation rates of cycled sorbents.

Figure 6. Comparison of experimental values of X_{CaSO_4} of Enguera (a) and Compostilla (b) limestones for N=20 and 50 with those calculated by means of the model and the average values shown in Table 2 (solid lines) (T=650 °C, SO₂ concentration=500 ppmv).

When applying the RPM model to design Ca-looping systems, it will be found that for the typically low sulfation conversions of solids in these systems, the particles will react mainly under the chemical controlled regime. Therefore the sulfation rate can be calculated by using the simplified form of Eq. 1 for this regime together with the parameters reported in Table 3:

$$\frac{dX}{dt} = \frac{k_s S C(1-X) \sqrt{1-\psi \ln(1-X)}}{(1-\varepsilon)} \quad (17)$$

The high reaction rate achieved for SO₂ capture under typical carbonator conditions in postcombustion Ca-looping systems, confirms that these reactors are suitable as SO₂ absorbers and as high-temperature CO₂ capture devices.

CONCLUSIONS

The random pore model has been applied to study the sulfation behaviour of cycled CaO particles at a temperature of 650° C (typical of carbonator reactors in Ca-looping CO₂ capture systems). Under these conditions, the sulfation proceeds through an initial chemically controlled step followed by second period where chemical reaction and diffusion through the product layer are the controlling resistances. Sulfation has been found to be a first reaction order with respect to SO₂ under the experimental conditions tested. The rate constants for surface reaction (k_s) between $4.32 \cdot 10^9$ and $5.63 \cdot 10^9$ m⁴/mol s were calculated at 650 °C for the three limestones used. The calculated values of effective product layer diffusivity (D) range from $2.43 \cdot 10^{-12}$ to $4.88 \cdot 10^{-12}$ m²/s. These values are in agreement with those found in the literature under similar conditions.

The results obtained with RPM indicate that cycled sorbents do not undergo pore plugging due to the growth of a layer of CaSO_4 (for reaction times of up to 20 min). For low CaO conversion ($X_{\text{CaSO}_4} < 0.05$), sulfation is a chemically controlled reaction. The high sulfation rates measured with highly cycled (carbonation-calcination) particles seem to indicate that post combustion Ca-looping carbonator reactors will be effective reactors for capturing SO_2 from flue gases.

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NOTATION

a, b	stoichiometric coefficients for carbonation reaction
C	concentration of CO_2 , kmol/m^3 ; b, bulk concentration; e, equilibrium
D	effective product layer diffusivity, m^2/s
D_0	pre-exponential factor in Eq. 16, m^2/s
E_{ak}	activation energy for the kinetic regime, kJ/mol
E_{aD}	activation energy for the combined diffusion and kinetic regime, kJ/mol
h	product layer thickness, m
k	sorbent deactivation constant
k_s	rate constant for surface reaction, m^4/mols
k_{s0}	pre-exponential factor in Eq. 15, m^4/mols
L	total length of pore system, m
M	molecular weight, kg/kmol
N	number of calcination/carbonation cycles
r_{pN}	radius of the pore after N cycles(m)
S	reaction surface per unit of volume, m^2/m^3
t	reaction time, s
V_M	molar volume, m^3/kmol
X_N	CaO molar conversion to CaCO_3 in each cycle
X_{CaSO_4}	CaO molar conversion to CaSO_4
X_r	residual CaO conversion
Z	ratio volume fraction after and before reaction
Greek letters	
β	$2 k_s a \rho (1 - \varepsilon) / M_{\text{CaO}} b D S$
ε	porosity
ρ	density, kg/m^3
ψ	$4\pi L(1 - \varepsilon) / S^2$
τ	$k_s C S t / (1 - \varepsilon)$

REFERENCES

1. Anthony EJ. Solid looping cycles: A new technology for coal conversion. *Ind. Eng. Chem. Res.* 2008; 47: 1747-1754.
2. Blamey J, Anthony EJ, Wang J, Fennel PS. The calcium looping cycle for large-scale CO₂ capture. *Progress in Energy and Combustion Science.* 2010; 36: 260-279.
3. Shimizu T, Hiramata T, Hosoda H, Kitano K, Inagaki M, Tejima K. A twin fluid-bed reactor for removal of CO₂ from combustion processes. *Trans IChemE.* 1999; 77: 62-68.
4. Romeo LM, Abanades JC, Escosa JM, Paño J, Jiménez A, Sánchez-Biezma A, Ballesteros JC. Oxyfuel carbonation/calcination cycle for low cost CO₂ capture in existing power plants. *Energy Conversion Management.* 2008; 49: 2809-2814.
5. Romano M. Coal-fired power plant with calcium oxide carbonation for post-combustion CO₂ capture. *Energy Procedia.* 2009; 1: 1099-1006.
6. Ströle J, Lasheras A, Galloy A, Epple B. Simulation of the carbonate looping process for post-combustion CO₂ capture from a coal-fired power plant. *Chem. Eng. Technol.* 2009; 32: 435-442.
7. Yongping Y, Rongrong Z, Liqiang D, Kavosh M, Patchigolla K, Oakey J. Integration and evaluation of a power plant with a CaO-based CO₂ capture system. *International Journal of Greenhouse Gas Control.* 2010; 4: 603-612.
8. Martínez I, Murillo R, Grasa G, Abanades JC. Integration of Ca looping system for CO₂ capture in existing power plants. *AIChE Journal.* 2010; doi 10.1002/aic.12461.
9. Anthony EJ, Granatstein DL. Sulfation phenomena in fluidized bed combustion systems. *Progress in Energy and Combustion Science.* 2001; 27: 215-236.

10. Li Y, Buchi S, Grace JR, Lim CJ. SO₂ removal and CO₂ capture by limestone resulting from calcination/sulfation/carbonation cycles. *Energy & Fuels*. 2005; 19: 1927-1934.
11. Ryu HJ, Grace JR, Lim CJ. Simultaneous CO₂/SO₂ capture characteristics of three limestones in a fluidized-bed reactor. *Energy & Fuels*. 2006; 20: 1621-1628.
12. Sun P, Grace JR, Lim CJ, Anthony EJ. Removal of CO₂ by calcium-based sorbents in presence of SO₂. *Energy & Fuels*. 2007; 21: 163-170.
13. Grasa GS, Alonso M, Abanades JC. Sulfation in a carbonation/calcination loop to capture CO₂. *Ind. Eng. Chem. Res.* 2008; 47: 1630-1635.
14. Manovic V, Anthony EJ. Sequential SO₂/CO₂ capture enhanced by steam reactivation of CaO-based sorbent. *Fuel*. 2008; 87: 1564-1573.
15. Manovic V, Anthony EJ, Loncarevic D. SO₂ retention by CaO-based sorbent spent in CO₂ looping cycles. *Ind. Eng. Chem. Res.* 2009; 48: 6617-6632.
16. Pacciani R, Müller CR, Davidson JF, Dennis JS, Hayhurst AN. Performance of novel synthetic Ca-based sorbent suitable for desulfurizing flue gases in a fluidized bed. *Ind. Eng. Chem. Res.* 2009; 48: 7016-7024.
17. Manovic M, Anthony EJ. Competition of sulphation and carbonation reactions during looping cycles for CO₂ capture by CaO-based sorbents. *J. Phys. Chem. A*. 2010; 114: 3397-4002.
18. Abanades JC, Anthony EJ, Wang J, Oakey JE. Fluidized bed combustion systems integrating CO₂ capture with CaO. *Env. Sci. Technol.* 2005; 39: 2861-2866.
19. Georgakis C, Chang CW, Szekely J. A changing grain size model for gas-solid reactions. *Chemical Engineering Science*. 1979; 34: 1072-1075.
20. Bhatia SK, Perlmutter DD. The effect of pore structure on fluid-solid reactions: Application to the SO₂-lime reaction. *AIChE Journal*. 1981; 27: 226-234.

21. Borgwardt RH, Bruce KR. Effect of specific surface area on the reactivity of CaO with SO₂. *AIChE Journal*. 1986; 32: 239-246.
22. Borgwardt RH, Bruce KR, Blake J. An investigation of product-layer diffusivity for CaO sulfation. *Ind. Eng. Chem. Res.* 1987; 26: 1993-1998.
23. Dennis JS, Hayhurst AN. Mechanism of the sulphation of calcined limestone particles in combustion gases. *Chemical Engineering Science*. 1990; 45: 1175-1187.
24. Hartman M, Coughlin RW. Reaction of sulfur dioxide with limestone and the grain model. *AIChE-Journal*. 1976; 22: 490-498.
25. Adánez J, García-Labiano F, Fierro V. Modelling for the high-temperature sulphation of calcium-based sorbents with cylindrical and plate-like geometries. *Chemical Engineering Science*. 2000; 55: 3665-3683.
26. Borgwardt RH. Kinetics of the reaction of SO₂ with calcined limestone. *Environmental Science Technology*. 1970; 4: 59-61.
27. Hartman M, Coughlin RW. Reaction of sulfur dioxide with limestone and the influence of pore structure. *Ind. Eng. Chem. Process Des. Develop.* 1974; 13: 248-253.
28. Pigford RL, Sliger G. Rate of diffusion-controlled reaction between gas and a porous solid sphere. Reaction of SO₂ with CaCO₃. *Ind. Eng. Chem. Process Des. Develop.* 1973; 12: 85-91.
29. Adánez J, Gayán P, García-Labiano F. Comparison of mechanistic models for the sulfation reaction in a broad range of particle sized of sorbents. *Ind. Eng. Chem. Res.* 1996; 35: 2190-2197.
30. Curran GP, Fink CE, Gorin E. CO₂ acceptor gasification process. Studies of acceptor properties. *Adv. Chem. Ser.* 1967; 69: 141-161.

31. Barker R. Reversibility of the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. J. Appl. Chem. Biotechnol. 1973; 23: 733-742.
32. Alvarez D, Abanades JC. Determination of the critical product layer thickness in the reaction of CaO with CO_2 . Ind. Eng. Chem. Res. 2005; 44: 5608-5615.
33. González B, Grasa GS, Alonso M, Abanades JC. Modeling of the Deactivation in a Carbonate loop at high temperatures calcination. Ind. Eng. Chem. Res. 2008; 45: 9256-9262.
34. Abanades JC. The maximum capture efficiency of CO_2 using a carbonation/calcination cycle of CaO/ CaCO_3 . Chemical Engineering Journal. 2002; 60: 303-306.
35. Abanades JC, Álvarez D. Conversion limits in the reaction of CO_2 with lime. Energy & Fuels. 2003; 17: 308-315.
36. Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: I. Isothermal, kinetic control. AIChE Journal. 1980; 26: 379-386.
37. Grasa G, Murillo R, Alonso M, Abanades JC. Application of the random pore model to the carbonation cyclic reaction. AIChE Journal. 2009; 55: 1246-1255.
38. Arias B, Abanades JC, Grasa GS. An analysis of the effect of carbonation conditions on CaO deactivation curves. Chemical Engineering Journal, 2011; 167: 255-261.
39. Grasa GS, Abanades JC. CO_2 capture capacity of CaO in long series of carbonation/calcination cycles. Ind. Eng. Chem. Res. 2006; 45: 8846-8851.

Figure 1. X_{CaSO_4} vs time for limestones used in this work after the first calcination (a) and 50 calcination/carbonation cycles (b) ($T=650\text{ }^{\circ}\text{C}$, SO_2 concentration=500ppmv).

Figure 2. Effect of the particle size on the sulfation of CaO after the first calcination (empty symbols) and 20 calcination/carbonation cycles (filled symbols) ($T=650\text{ }^{\circ}\text{C}$, SO_2 concentration=500ppmv).

Figure 3. Effect of SO_2 concentration on X_{CaSO_4} for the fresh calcined Compostilla limestone ($N=1$) ($T=650^\circ\text{C}$) (a) and the maximum reaction rate vs SO_2 concentration (b).

Figure 4. Fitting of Eq. 4 (a) and 5 (b) to the experimental data obtained for the Enguera limestone at N=20 ($T=650\text{ }^{\circ}\text{C}$, $C_{\text{SO}_2}=500\text{ ppmv}$).

Figure 5. Comparison of experimental and calculated values of X_{CaSO_4} for Compostilla limestone with different numbers of cycles ($T=650\text{ }^{\circ}\text{C}$, $C_{SO_2}=500\text{ ppmv}$) (calculated values-solid lines).

Figure 6. Comparison of experimental values of X_{CaSO_4} of Enguera and Compostilla limestones for $N=20$ and 50 with those calculated by means of the model and the average values shown in Table 2 (solid lines) ($T=650\text{ }^{\circ}\text{C}$, $C_{SO_2}=500\text{ ppmv}$).