A KINETICS STUDY ON THE SORPTION OF SO$_2$ BY LIMESTONE THROUGH THERMOGRAVIMETRY

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Abstract. Thermogravimetry is applied to determine the effect of temperature and atmosphere on conversion and kinetics of SO$_2$ sorption by limestone. Ranges of temperature and particle size were applied that are typical of the fluidized bed coal combustion. Isothermal experiments were performed for different temperatures (between 650 and 950 ^{o}C), at local atmospheric pressure (~ 697 mmHg), in dynamic atmospheres of air and nitrogen. The results of sulfation were evaluated using Arrhenius' kinetics. The resulting activation energies (4.446 kJ mol^{-1} in air and 3.748 kJ mol^{-1} in nitrogen) suggest the reaction to be controlled by Knudsen diffusion. An effectiveness parameter was defined as the ratio between the instantaneous reaction rate coefficient and its maximum value, indicating the time decay of reactivity as sulfation advances. The average effectiveness was determined for all the temperatures considering the whole sulfation time interval, which was always around 200 seconds. The highest values of average effectiveness were found at 800 ^{o}C in air atmosphere (0.2854), and 900 ^{o}C in nitrogen atmosphere (0.3142). Optimum conversion resulted between 800 and 850 ^{o}C in air, and around 900 ^{o}C in nitrogen.

Keywords: *thermogravimetry, sulfation, limestone, sulfur dioxide, chemical kinetcs.*
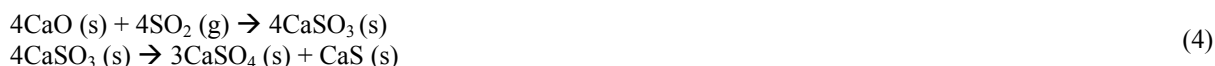
1. Introduction

Mineral 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 SO$_2$ emission into earth's atmosphere (Li and Sadakata, 1999). Limestone sorbents are largely used for SO$_2$ removal form combustion gases. In fluidized bed combustion, for instance, limestone is injected directly into the combustion chamber, providing for "in locus" sorption of SO$_2$ (Van Houte and Delmon, 1979).

The kinetics of SO$_2$ sorption by limestone may be studied through thermal analysis, under the application of suitable kinetic models. There is considerable discussion in literature concerning the suitability of different kinetic models for reactive processes of complex materials such as limestone (Burnham and Braun, 1987). When submitted to high temperatures, limestone decomposes into a solid mostly formed of CaO and CO$_2$. The calcination reaction is shown in Eq. (1).

$$CaCO_3 \, (s) \rightarrow CaO \, (s) + CO_2 \, (g) \qquad \Delta H = + 182.1 \text{ kJ g}^{-1} \text{ mol}^{-1} \qquad (1)$$
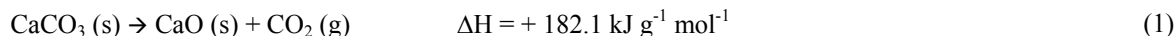
The formed calcine is very porous and has the same size of the original limestone, so that its high porosity is due to the difference between the molar volumes of CaCO$_3$ (~ 36.9 cm^3 mol^{-1}) and CaO (~16.9 cm^3 mol^{-1}) (Hartman and Coughlin, 1976, Simons et al., 1987, Dam-Johansen and Ostergaard, 1991). Depending on temperature and SO$_2$ partial pressure, different chemical species may be produced from the reaction between CaO and SO$_2$. The most commonly assumed routes for sulfuation are:

$$\begin{aligned} CaO \, (s) + SO_2 \, (g) &\rightarrow CaSO_3 \, (s) \\ CaSO_3 \, (s) + \tfrac{1}{2} \, O_2 \, (g) &\rightarrow CaSO_4 \, (s) \end{aligned} \qquad (2)$$

$$\begin{aligned} SO_2 \, (g) + \tfrac{1}{2} \, O_2 \, (g) &\rightarrow SO_3 \, (g) \\ CaO \, (s) + SO_3 \, (g) &\rightarrow CaSO_4 \, (s) \end{aligned} \qquad (3)$$

$$\begin{aligned} 4CaO \, (s) + 4SO_2 \, (g) &\rightarrow 4CaSO_3 \, (s) \\ 4CaSO_3 \, (s) &\rightarrow 3CaSO_4 \, (s) + CaS \, (s) \end{aligned} \qquad (4)$$

As observed by Dennis and Hayhurst (1990), routes (2) and (3) were proposed by Moss (1975). Route (4) was proposed by Low et al. (1971). As remarked by Anthony and Granatstein (2001), Moss suggested that the reactions of route (2) predominate at low temperatures where $CaSO_3$ is stable, while the reactions of route (3) predominate at high temperatures (>850 ^{o}C) where $CaSO_3$ becomes unstable.

During sulfation the pores of the CaO particle are filled with products ($CaSO_4$, $CaSO_3$, CaS), and become progressively plugged. Even compared to the natural limestone, the physical structure of the sulfated particle becomes more compact owing to the difference between the molar volumes of $CaSO_4$ (~ 46 cm^3 mol^{-1}) and $CaCO_3$ (~36.9 cm^3 mol^{-1}) (Dam-Johansen and Ostergaard, 1991).

Limestone sulfation is affected by porosity, size and size distribution of pores, intra-particle superficial area (Borgwardt and Bruce, 1986, Adánez et al., 1993, Li and Sadakata, 1999), geological age, size and density of the particles (Yrjas et al., 1995). Another factor to consider is the presence of chemical elements that may act as catalysts or poisons (Dam-Johansen and Ostegaard, 1991). The first works showing the influence of internal pore structure on CaO reaction to SO_2 were performed in the early 70's. Whit that intrinsic physical features started to be considered alongside with the usual external superficial effects (Borgwardt and Bruce, 1986). In one of the first works, Pigford and Sliger (1973) found that in 96 µm limestone particles there was significant resistance to intra-particle gas diffusion at 980 ^{o}C. The authors concluded that SO_2 diffusion through the $CaSO_4$ product layers controlled sulfation rate. Borgwardt and Harvey (1972) evaluated the effect of porosity on sulfation. They defined an effectiveness factor as the ratio between the observed reaction rate, and its theoretical value if the whole particle volume was available for reaction. A strong dependence between effectiveness and pore structure was observed (volume, area and shape). The authors concluded that the effectiveness was dependent on the external layers pore plugging by $CaSO_4$, thereby imposing loss of internal superficial area, and turning the CaO of more internal layers inaccessible.

The search for reaction controlling steps and kinetic parameters for SO_2 sorption by limestones has been undertaken by various researchers. Commonly reported activation energies vary in a wide range, from unities to hundreds of kJ mol^{-1}. Several works report activation energies obtained through thermogravimetry in various operational conditions, e.g.: 133 kJ mol^{-1} between 650 and 800 ^{o}C (Iisa and Hupa, 1992); 146 kJ mol^{-1} for conversion above 50 % (Hajaligol et al., 1988); 64 kJ mol^{-1} for direct sulfation, and 205 kJ mol^{-1} for sulfation preceded of calcination (Snow et al., 1988); 95±14, 77±20 and 70±21 kJ mol^{-1} for direct sulfation in atmospheres containing, respectively, 30, 50 and 80 % CO_2, between 500 and 850 ^{o}C (Tullin et al., 1993). Crnkovic (2003) applied thermogravimetry to evaluate the sulfation of a calcitic and a dolomitic limestone. Samples of particulate with sizes between 390 and 779 µm were submitted to process temperatures between 600 and 900 ^{o}C. In the sulfation of the dolomitc previously calcined 650 µm limestone, in SO_2 atmosphere, the apparent activation energy at the maximum reaction rate condition resulted 5.3 kJ mol^{-1} (between 600 and 700 ^{o}C), and 11.6 kJ mol^{-1} (between 700 and 850 ^{o}C).

The activation energy in heterogeneous fluid-solid reactions is commonly addressed as apparent since it is highly affected by intra-particle mass transport. Pore plugging, sintering and particle size become crucial (James and Hughes, 1976, Iisa and Hupa, 1992, Crnkovic, 2003). Fuertes et al. (1994) notes a literature agreement (Bhatia and Permutter, 1981, Pigford and Sliger, 1973, Gopalakrishanan and Seehra, 1990) on that the high reported activation energies for calcine sulfation (between 121 and 167 kJ mol^{-1}) are not satisfactorily explained by diffusion control. They observe that under molecular diffusion control the activation energies result around 12 kJ mol^{-1}, while under Knudsen diffusion control they result around 4 kJ mol^{-1}.

Dennis and Hayhurst (1990) determined conversions and reaction rate coefficients for the sorption of SO_2 by limestone in a fluidized bed reactor electrically heated, in atmospheres containing variable concentrations of O_2 and N_2. They found that by decreasing O_2 concentration conversion increases, while the reaction rate coefficient decreases slower in time. The authors concluded, however, that the presence of a small amount of O_2 accelerates the sulfation without causing significant decrease on conversion. Lindo (2003) studied the effect of the concentration of SO_2 on calcination and sulfation of limestones in a fluidized bed reactor. The author found a quicker and more effective calcination when SO_2 was present in higher concentrations. Supposedly, at higher concentrations of SO_2 pore plugging is intensified at the outer layers of the particles, forming thinner sulfated shells. Those would be cracked as CO_2 flows out of the particles, leaving a path for SO_2 penetration. Costa (2000) studied the effect of temperature on conversion and reaction rate coefficient for the sorption of SO_2 by limestone in a fluidized bed. The author used the same limestone applied in this study, in two sizes (545 and 650 µm). The reaction rate coefficient for the 650 µm limestone resulted maximum at 881 ^{o}C.

In this work thermogravimetry is applied to determine the effect of temperature and atmosphere on conversion and kinetics of SO_2 sorption by limestone. Ranges of temperature and particle size were applied that are typical of the fluidized bed coal combustion.

2. Experiments

The experiments were performed in a Shidadzu TGA-5H thermogravimetric analyzer. A calcitic limestone from Itaú-MG was used. Samples of 10 mg of natural limestone of 545 µm mean size were used. Previously to the sulfation experiments, the limestone was calcined inside the analyzer in air or nitrogen atmospheres (80 mL min^{-1}) applying a heating rate of 30 ^{o}C min^{-1} until the thermal decomposition was completed, and the temperature for the sulfation experiment was reached. This condition was kept for 20 min. Then SO_2 was added to the atmosphere (20 mL min^{-1}) and the isothermal sulfation developed. Five different sulfation temperatures were applied (750, 800, 850, 900and950 ^{o}C),

and each experiment was repeated 4 times. The experimental conditions choice is described in Crnkovic (2003) and Ávila (2005).

3. Methodology

Arrhenius kinetics is applied. Therefore, the reaction rate coefficient is given by:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

where A is the pré-exponential or frequency factor, E_a is the apparent activation energy, R is the ideal gas constant, and T is the temperature. The reaction rate may be given by:

$$-\frac{dm}{dt} \propto m^a \, C_{SO_2}^b \, C_{O_2}^c \tag{6}$$

where m is the mass of Ca plus Mg available for sulfation, dm/dt is the reaction rate of Ca plus Mg, C is the concentration of gases (SO_2 and O_2) in the atmosphere, and (a, b, c) represent the order of the global reaction in relation to m and C. First order reaction is considered regarding the mass of the sample, and the reaction is assumed to be independent on the concentration of reaction gases. Then, the reaction is assumed of order zero regarding the concentrations of reacting gases (differential conditions are applied). Under those assumptions, the reaction rate becomes:

$$-\frac{dm}{dt} \propto m \tag{7}$$

Introducing a reaction rate coefficient (k) in Eq. (7), it comes:

$$-\frac{dm}{dt} = k \, m \, . \tag{8}$$

From Eqs. (7) and (8), and introducing a natural logarithm operator:

$$\ln\left[-\frac{1}{m}\frac{dm}{dt}\right] = \ln A - \frac{E_a}{R}\frac{1}{T} \tag{9}$$

Through a mass balance, and assuming that Ca and Mg are consumed at the same rate, the available mass of Ca plus Mg available for reaction can be found as:

$$m = M_A\left(Y_{Ca} + Y_{Mg}\right) - \left\{\left(M_s - M_c\right)\cdot\left[\frac{\left(W_{Ca}Y_{Ca} + W_{Mg}Y_{Mg}\right)}{\left(W_{SO_2} + \frac{1}{2}W_{O_2}\right)\cdot\left(Y_{Ca} + Y_{Mg}\right)}\right]\right\}. \tag{10}$$

where M_A is the initial sample mass of natural limestone, M_S is the mass of sulfated limestone, M_C is the mass of the sample after calcination, Y stands for the mass fraction of Ca and Mg in the natural limestone, and W is the molar mass of the various species. From Eq. (10), the rate of reaction of Ca plus Mg results:

$$\frac{dm}{dt} = -\left[\frac{\left(W_{Ca}Y_{Ca} + W_{Mg}Y_{Mg}\right)}{\left(W_{SO_2} + \frac{1}{2}W_{O_2}\right)\cdot\left(Y_{Ca} + Y_{Mg}\right)}\right]\frac{dM_s}{dt} \tag{11}$$

From the empirical data and applying Eq. (8) an Arrhenius plot is defined. Then, by linear regression both the pre-exponential factor and the activation energy are determined.

In the present work an effectiveness factor (η) is defined as the ratio between the reaction rate coefficient and its maximum temporal value (k_{max}). Such effectiveness represents a decay on reaction rate in time, and is given by:

$$\eta = \frac{k}{k_{max}} = \frac{\left[-\dfrac{1}{m}\dfrac{dm}{dt}\right]}{\left[-\dfrac{1}{m}\dfrac{dm}{dt}\right]_{max}} \qquad (12)$$

Conversion (X) is defined as the ratio between the number of moles of SO_2 sorbed and the number of moles of Ca plus Mg in the sample. From a mass balance it comes that:

$$X = \frac{\dfrac{M_F - M_C}{W_{so_2} + W_{1/2O_2}}}{M_A\left(\dfrac{Y_{Ca}}{W_{Ca}} + \dfrac{Y_{Mg}}{W_{Mg}}\right)} \, x \, 100 \qquad (13)$$

where M_F is the final sample mass after sulfation is finished.

The required values of M_A, M_s, M_c and dM/dt are determined from the thermogravimetric experiments. The mass fractions of Ca and Mg in the limestone, and the molecular weights of the concerning species are given in Tab. 1.

Table 1. Mass fractions of Ca and Mg in the limestone, and molecular weights

Y_{Ca}	Y_{Mg}	W_{Ca}	W_{Mg}	W_{SO2}	W_{O2}
0,3534	0,0035	40,078	24,305	64,064	31,998

4. Results

Figure 1 presents the results of the 4 sulfation experiments performed for one of the considered temperatures (900 °C) in nitrogen atmosphere. The sets of curves for all the other experiments resulted similar. The curves in Fig. 1 show both the calcination and the sulfation events. The elevations observed in the TG curves during the heating stage towards the calcination event are possibly due to drag of the flowing atmosphere over the sample, and do not affect the present sulfation analysis.
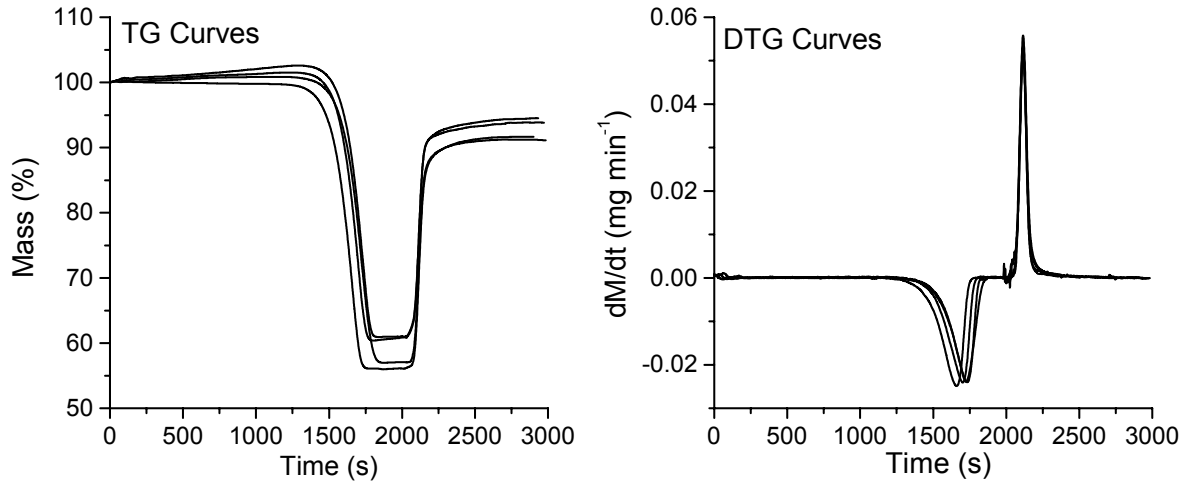

Figure 1. TG and DTG curves for limestone sulfation at 900 °C in nitrogen atmosphere (results of 4 experiments)

Figure 2 shows the Arrhenius plots derived from the empirical data for both air and nitrogen atmospheres. In the experiments in air the reaction rate increased with temperature until 850 °C, and considerably dropped above that. This behavior is clearly seen in Fig. (2), and indicates a change on reaction mechanism possibly due to sintering of the limestone. For this case, the analysis was performed for temperatures up to 850 °C, and additional experiments were performed at 650 and 700 °C. From the Arrhenius plots of Fig. (2), it comes that:

$$k_{max}(T) = 0.822\,exp\left(\frac{4.446}{RT}\right) \text{ in air atmosphere}$$

and

$$k_{max}(T) = 1.071\,exp\left(\frac{3.748}{RT}\right) \text{ in nitrogen atmosphere}$$

As seen, both the pre-exponential factor and the activation energy resulted close as the atmosphere was switched from nitrogen to air. The values found for the activation energy are at the order of those usual for sulfation under Knudsen diffusion control (i.e. 4 kJ mol^{-1}, Fuertes et al., 1994).
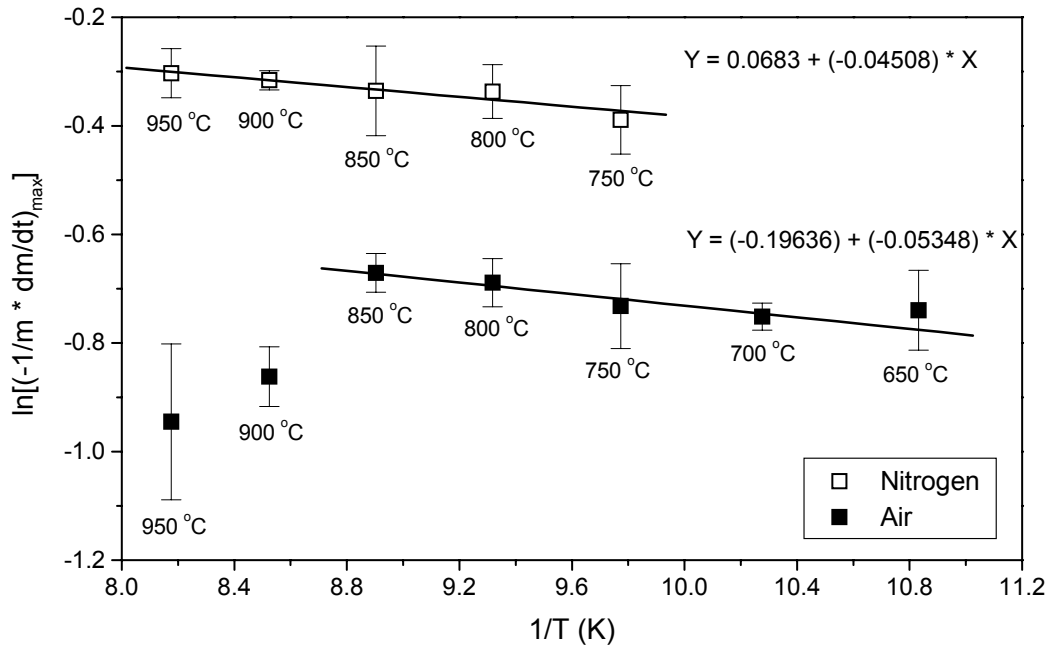

Figure 2. Arrhenius plots for the sulfation of limestone in air and nitrogen atmospheres
(the bars indicate the standard deviation around the average of 4 experiments)

The graphs of Fig. 3 show the effectiveness for all the experiments in the applied temperatures, for the atmospheres of air and nitrogen. It is seen that temperature has little effect on effectiveness, and that very similar profiles are found in both atmospheres. All the curves are quite symmetric. This means that the rate of grown in effectiveness towards the maximum is similar to the following decay as sulfation comes to the end. The grown step corresponds to the time interval required for the reactive gas to diffuse inside the particles until the instant in which the maximum effectiveness is reached. The following decay step corresponds to the time interval in which pore plugging progressively limits reaction. The symmetry of the curves is quite reasonable since in both the grown and the decay steps intra-particle gas diffusion sets the velocity of reaction.
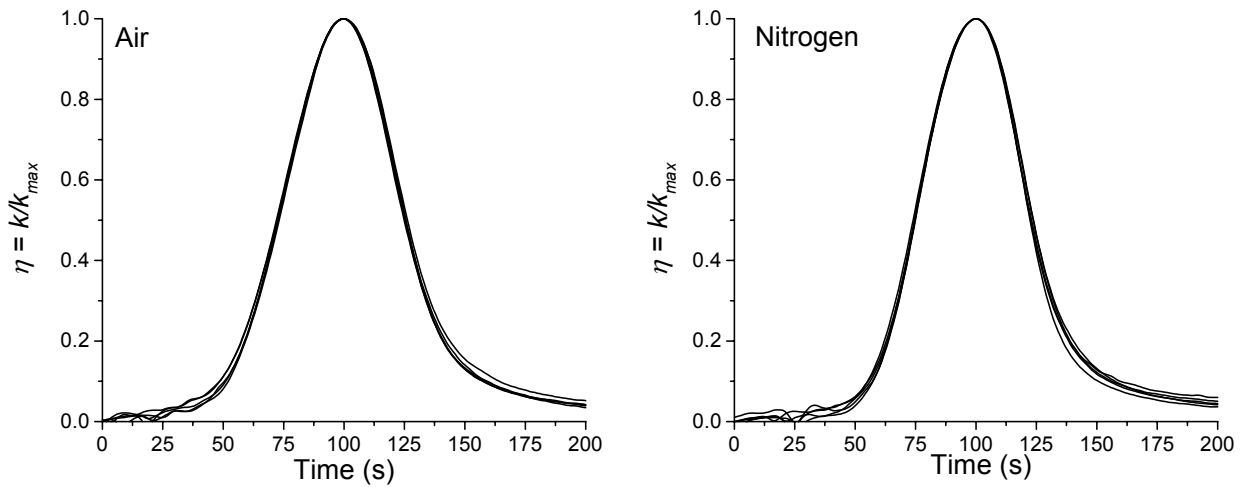

Figure 3. Effectiveness for all the experiments in all the temperatures, for the atmospheres of air and nitrogen

Figure 4 presents the time averaged effectiveness as a function of temperature, in both air and nitrogen atmospheres. For all the considered temperatures the averaged effectiveness resulted slightly higher in nitrogen

atmosphere. The presence of oxygen in the air atmosphere seems to impose a slight reductive effect on reaction rate. The maximum averaged effectiveness was found at 800 ^{o}C in air atmosphere (0,2854), and at 900 ^{o}C in nitrogen atmosphere (0,3142).
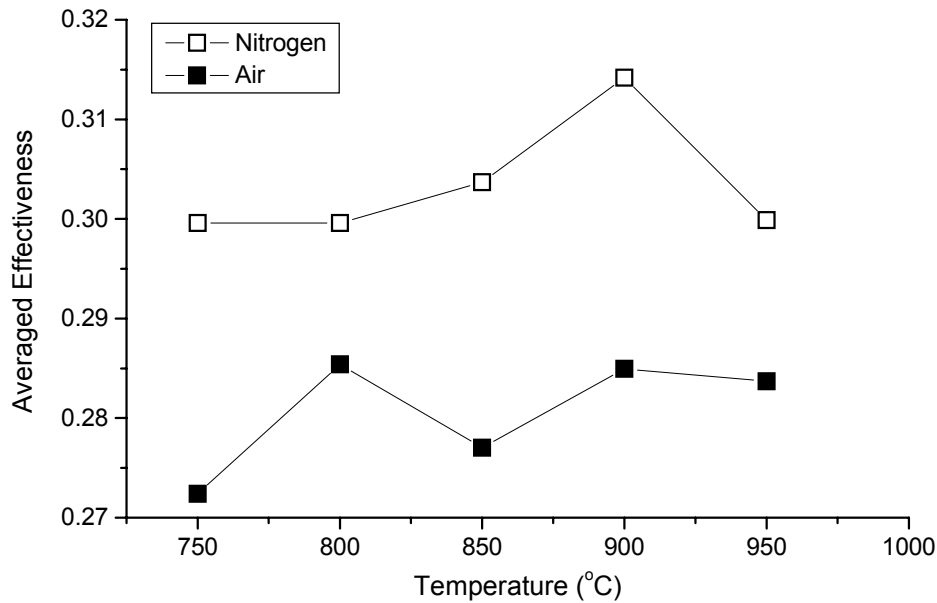

Figure 4. Time averaged effectiveness as a function of temperature, in both air and nitrogen atmospheres

Figure 5 shows the conversions as a function of temperature in air and nitrogen atmospheres. In both atmospheres conversion grows with temperature and then starts to drop as temperature further increases. This indicates that the reaction mechanism is changing possibly due to sintering of the limestone. The maximum conversion was found between 800 and 850 ^{o}C for air atmosphere, and around 900 ^{o}C in atmosphere of nitrogen.
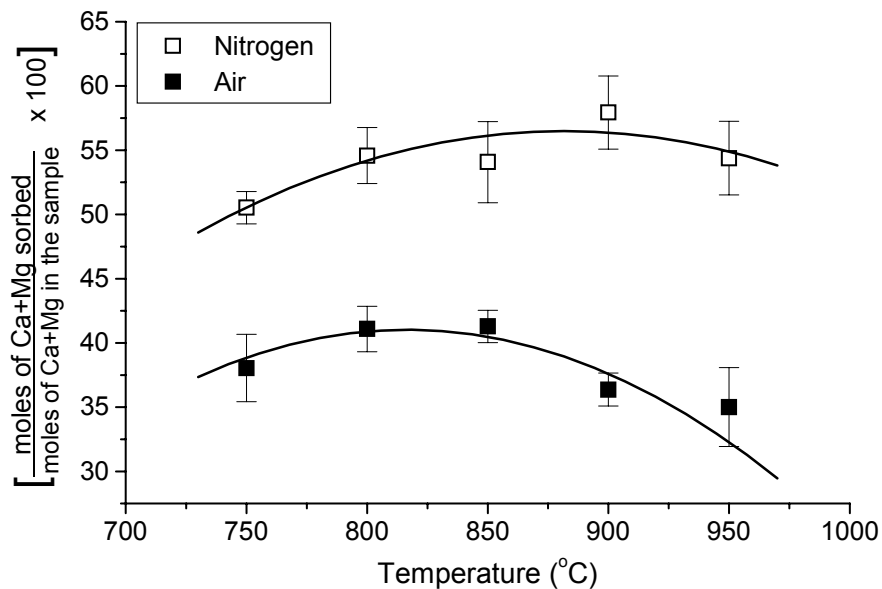

Figure 5. Conversion as a function of temperature, in both air and nitrogen atmospheres
(the bars indicate the standard deviation around the average of 4 experiments)

5. Conclusions

The kinetic parameters for both the applied atmospheres resulted very close. The presence of oxygen in the air atmosphere caused a slight reductive effect on reaction rate, the pre-exponential factor resulted slightly lower and the activation energy slightly higher. The values found for the activation energy are at the order of those usual for sulfation under Knudsen diffusion control.

The effectiveness was not considerably affected by temperature, and resulted very close in both atmospheres. The profiles in time resulted very symmetric since in both the grown and the decay stages intra-particle gas diffusion sets the velocity of reaction. The averaged effectiveness resulted slightly higher in nitrogen atmosphere. The maximum averaged effectiveness was found at 800 ^{o}C in air atmosphere (0,2854), and at 900 ^{o}C in nitrogen atmosphere (0,3142).

Conversion grew with temperature and then started to drop as temperature was further increased, in both atmospheres. A change in reaction mechanism accounts for that possibly due to sintering of the limestone. The maximum conversion was found between 800 and 850 ^{o}C for air atmosphere, and around 900 ^{o}C in atmosphere of nitrogen.

6. Acknowledgements

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