Original Research Article

Desulfurization of flue gases using materials based on $Ca(OH)_2$ supported on clays

ABSTRACT

Acid rain is a worldwide environmental problem that started in industrialized countries, and it has been extended to underdeveloped countries. Actions must be taken, and one of those is to deal with one of the major SO_2 emission sources that are thermal power plants. A way of decreasing the SO_2 emissions is to treat the flue gases with sorbent materials, which selectively trap the SO_2. These materials may be based on calcium and many efforts have been recently performed in order to increase their activity and yield. In the present work, SO_2 sorbent materials, based on $Ca(OH)_2$ at different mass ratios, were prepared supported on clays (bentonite and tonsil), and their activity was tested in a thermogravimetric balance. In addition, ultrasonic energy was applied during preparation trying to improve their performance. It was found that activity increased proportional to the Ca load. Also, when temperature increased from 350 to 450°C, the SO_2 sorption capacity increased. The support clays did not play an important role; at low temperature, activity was slightly better in materials supported on tonsil, but as temperature increased the yield of materials supported on bentonite surpassed those of material supported on tonsil. Ultrasonic energy did not improve the performance of sorbent materials, and, in fact, the sorption capacity diminished when ultrasonic energy was applied during preparation of materials. Finally, the SO_2 sorption process was modeled using a modified shrinking core approach and kinetics parameters were estimated.

Keywords: acid rain, $Ca(OH)_2$, tonsil, bentonite, sorbent materials, flue gas desulfurization, ultrasonic energy, kinetics parameter estimation

1. INTRODUCTION

The combustion of fossil fuel for the generation and/or transformation of energy in sectors, such as, industry, transport and commercial has caused an increase in the concentrations of gaseous and particulate pollutants in the atmosphere. This increase in pollutants has resulted in air pollution. One of the most critical environmental problems is the acid rain, which is a broad term that describes several ways through which acid falls out, including acidic rain, fog, hail and snow. At the beginning of the problem, acidic rainfall was commonly detected around industrial areas; however, with the increased use of tall stacks for power plants and industries, atmospheric emissions are now transported beyond the industrial areas. Acid rain is the result of many steps of chemical reactions between air borne pollutants (oxides of sulfur, nitrogen and other constituents present in the atmosphere) and atmospheric water and oxygen. Main sources of these oxides are fossil fuel fired power stations and smelters for SO_2, and motor vehicle exhausts for NO_X. These oxides may react with other chemicals and produce corrosive substances that are washed out either in wet or dry form by rain as acid deposition [1-3].

Acid rain has several effects in the ecosystem, which include the decay in growth of trees, crops, aquatic flora and fauna. In addition, soil fertility is deteriorated as a result of leaching of nutrient cations and the increased availability of toxic heavy metals. Also, stones, metals, paints, textiles and ceramics can be eroded and corroded due to acid rain. It can also indirectly affect human health since it has been shown that SO_2 and NO_x contribute to the formation of $PM_{2,5}$ [3-6]. The acid rain problem has been tackled to some extent in developed countries by reducing the emission of the precursor gases, and several actions have been created in different parts of the world i.e., the Gothenburg

Protocol for the European Union and the US Acid Rain Program in the Title IV of the 1990 Clean Air Act Amendments. [7-10].

Due to the rapid economic development and energy consumption throughout the world, fossil fuel consumption has significantly increased during the last few decades. The use of fossil fuel is the major cause of large-scale generation of acid precursors in the atmosphere. The problem was originally identified as an issue in developed countries, but with the increase in industrialization and urbanization, developing countries are now also experiencing this issue.

Many reviews have been published related to commercial and pilot-plant technologies for the abatement of SO_2 from thermal power plants [11-13]. Most of the probed technologies are based in calcium sorbents, such as, $Ca(OH)_2$ and CaO, either in wet or dry conditions. New research efforts have been addressed to improve the yield of calcium materials as SO_2 sorbent by mixing it with several supports, such as, silica, fly ash, blast furnace slag, clays, and activated carbon [14-21]. In the present work $Ca(OH)_2$ was mixed with bentonite and tonsil at many mass ratios. These clays were chosen because they are abundant in Mexico and can be considered a local low-cost raw material, which would reduce the operating cost if they were applied in a local power plant. Bentonite is an aluminiumhydrosilicate, in which the proportion of silicic acid to alumina is about 4:1. On the other hand, tonsil is created from bentonite by acid activation. During this activation, the individual layers are attacked by the acid; as result, aluminum, iron, calcium and magnesium ions are released from the lattice. Also, in a way for further improvement the performance of the sorbent materials, ultrasonic energy may be applied during preparation in an effort to reduce the particle size and increase available active sites as it has occurred in other materials [22-26].

2. MATERIAL AND METHODS

2.1. Sorbent Preparation

Samples of $Ca(OH)_2$ supported in bentonite and tonsil were synthesized by preparing slurries at different mass ratio. Some of them were mechanically stirred during 4 h at 60-70°C. In other slurries, ultrasonic energy was applied during 4 h maintaining the temperature below 70°C. After the mixing, slurries were dried overnight a 120°C and pulverized.

2.2. Sorbent characterization

To determine the actual calcium content, samples of the sorbent-materials were analyzed by Atomic Absorption Spectroscopy. Table 1 presents the composition of the different materials.

Table 1. Calcium composition in the prepared sorbent materials.

Material	$Ca(OH)_2$ content [wt%]
Ca-Bentonite 1:2 MS	30.7505
Ca-Tonsil 1:2 MS	34.4440
Ca-Bentonite 1:1 MS	47.7199
Ca-Tonsil 1:1 MS	51.9835
Ca-Bentonite 2:1 MS	67.9053
Ca-Tonsil 2:1 MS	68.0212
Ca-Bentonite 1:2 UE	30.3809
Ca-Tonsil 1:2 UE	32.0253
Ca-Bentonite 1:1 UE	49.7233
Ca-Tonsil 1:1 UE	51.2866
Ca-Bentonite 2:1 UE	64.3171
Ca-Tonsil 2:1 UE	63.6533

MS: Mechanical Stirring

UE: Ultrasonic Energy

2.3. Sulfation of sorbents

The sulfation of the materials was carried out in a thermogravimetric balance (TA Instruments 2050) by passing a stream of certified 3600 ppm_v SO_2/N_2 through a known amount of sorbent material. The gas flow rate was 100 mL/min, which is the maximum flow of the thermobalance. The gain of weight in the material was assigned to the sorption of SO_2 on the active sites.

3. RESULTS AND DISCUSSION

3.1. Sorption of SO_2 on bentonite and tonsil

Experiments in the TGA varying temperature (heating rate: 10°C/min) were performed to check if supports were able to adsorb SO_2. Results are presented in Fig. 1, and it was observed that none of the clays retained SO_2. In fact, it was noticed that weight loss occurred as the temperature increased; however, this is attributed to a loss of humidity in the interval between room temperature and 120°C. Then, a drastic weight loss was observed, especially in bentonite, at temperatures higher than 550°C; this is a result of the thermal rearrangement of the crystalline structure.

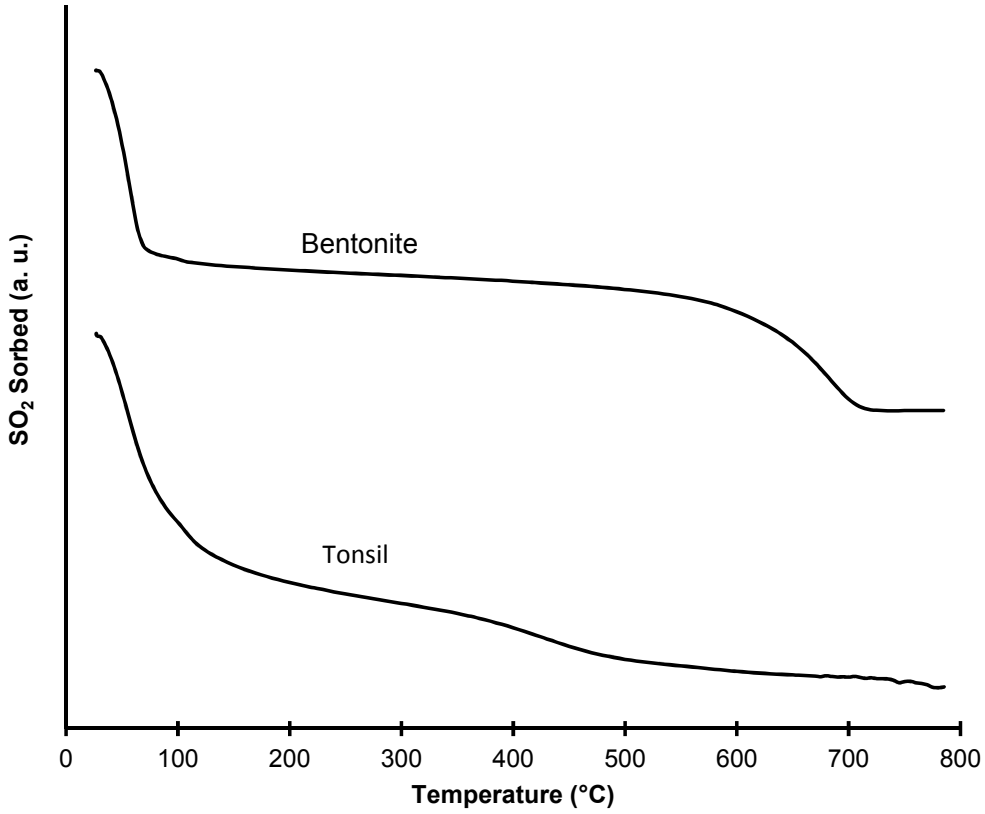

Figure 1. Thermogravimetric profiles of the supports in the sulfurization process at variable temperature.

3.2. Effect of temperature in the sorption capacity

To determine the temperature interval in which the sorbents were studied, an experiment in the TGA with pure $Ca(OH)_2$ at heating rate of 10°C/min was performed. The result is shown in Fig. 2. It is observed that the SO_2 sorption process begins at 300°C, and it continues up to 650°C. At temperature interval of 420-480°C is noted a drastic loss of weight, but it can be assigned to $Ca(OH)_2$ decomposition to form CaO, which is also active for adsorbing SO_2. Finally, the selected temperature

interval was 350-450°C since at this temperature interval the flue gases enter and exit the preheaters in a thermal power plant, and the proposed technology would be installed at this point.

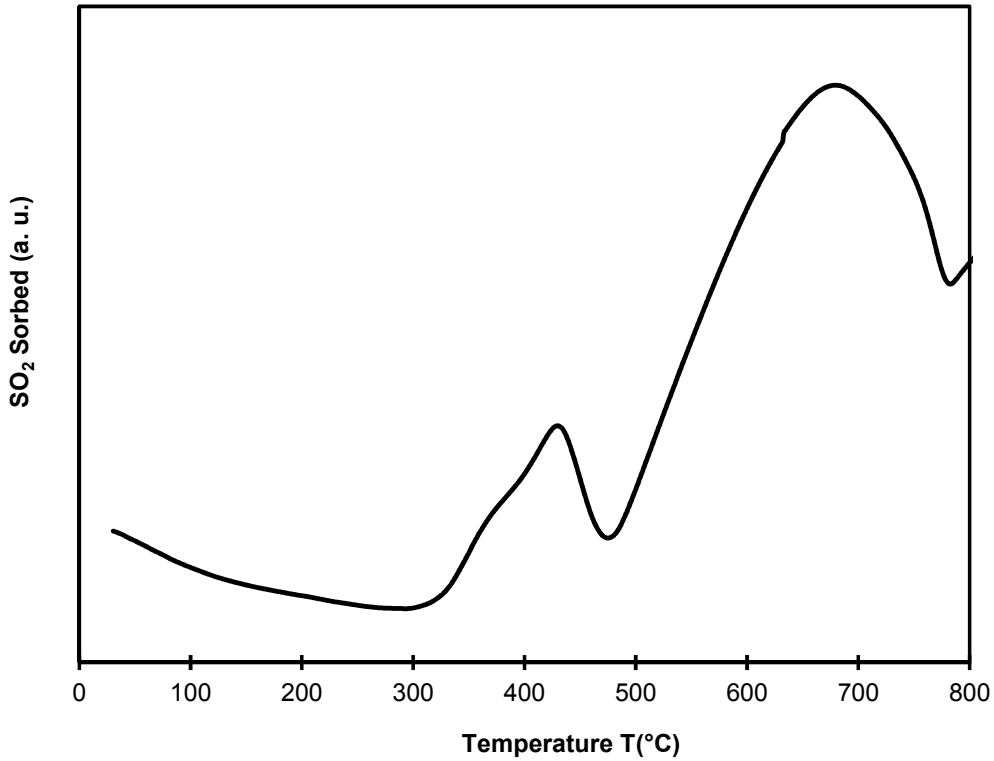

Fig. 2. Thermogravimetric profiles of pure $Ca(OH)_2$ in the sulfurization process at variable temperature.

Experiments were carried out at constant temperature for 90 min and the amount of SO_2 sorbed in the prepared materials is presented in Fig. 3. It is clearly noticed that as the temperature increases, the sorption capacity of the materials is enhanced. This effect is observed in all materials regardless of the support, Ca load, or preparation method.

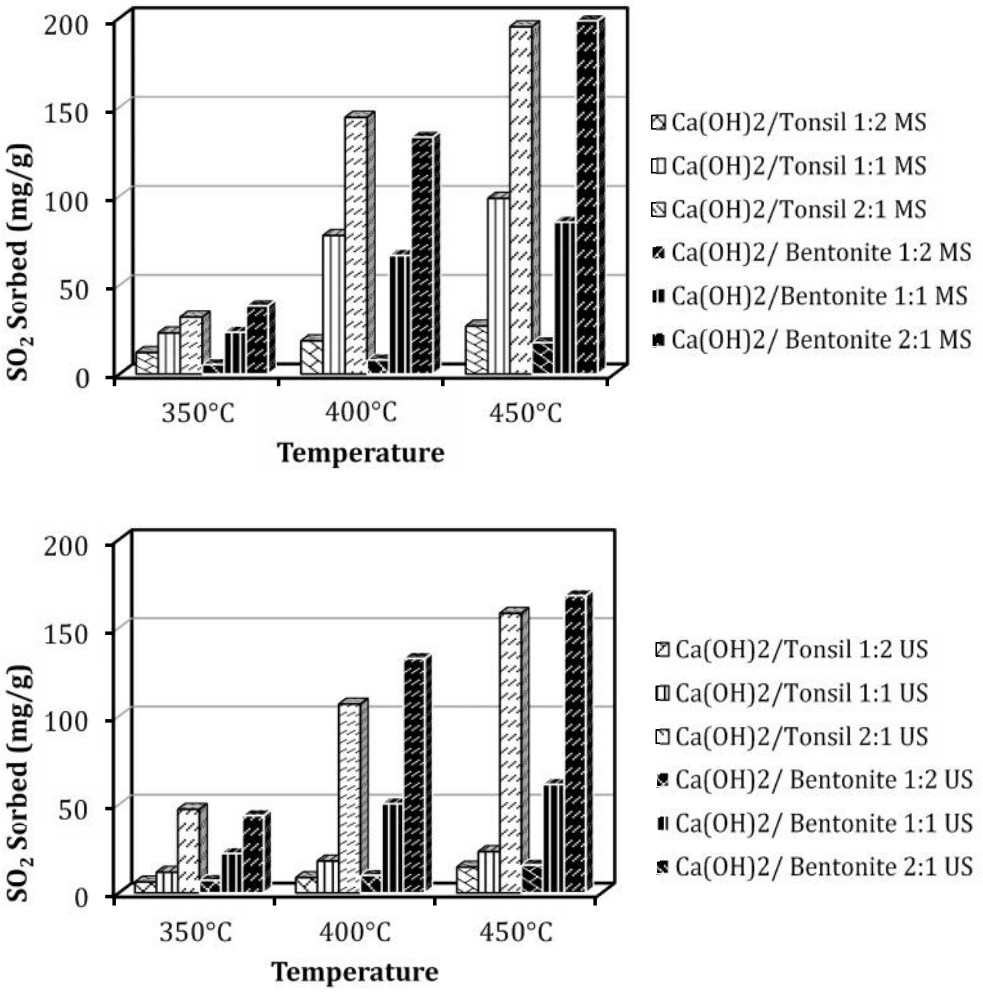

Fig. 3. SO_2 sorption capacity of the different prepared materials at 90 min.

3.3. Effect of calcium load

According to the results presented in Fig. 4, Ca load plays an important role in the sorption capacity of the prepared materials as it has been previously reported [Liu et al., 2004; Macias-Perez et al., 2007; Lin et al., 2003]. At lower temperature (350°C) the effect is not well-defined, but as the temperature increases it is observed that Ca load enhances this property. For instance, at 450°C, and considering the material supported on tonsil and prepared with mechanical stirring, at Ca load of 31 wt%, the sorption capacity is 27 mg/g, but as the Ca load increases to 52 wt% (1.7 times), the sorption capacity rises up to 98 mg/g, which is 3.6 times more than at 31 wt %. Moreover, when Ca load is 68 wt% (1.3 times with respect to the last load), the sorption capacity increases 2 times compared to the last load, sorbing 194 mg/g. These results are unexpected; it seems that supports (either tonsil or bentonite) are blocking the active sites instead of providing better dispersion and more active sites. Similar results were previously reported in materials supported on fly ash at low Ca loads [27].

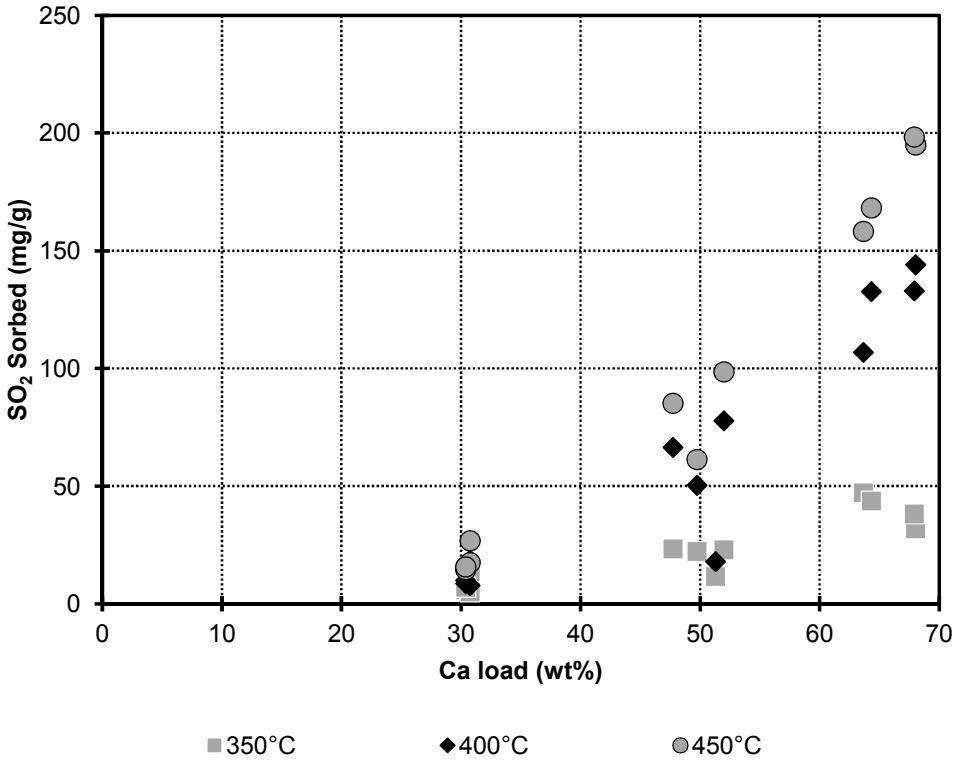

Fig. 4. Effect of calcium load in the SO_2 sorption capacity of the prepared materials.

3.4. Effect of support

The type of support did not show a trend, considering the results presented in Fig. 3. Data suggest that at low Ca loads the materials supported on tonsil result in slightly better yields, but as temperature and Ca load increased this tendency disappears, and finally, at higher temperature (450°C) and Ca load, the better performance was obtained for the material supported on bentonite regardless of preparation method.

3.5. Effect of preparation method

Ultrasonic energy was used trying to improve the yield of the proposed materials. Since the application of ultrasonic materials in slurries is able to fragment the solid particles, decreasing their size, it is proposed that this event would multiply the number of available active sites for the SO_2 sorption process. Nevertheless, the results presented in Fig. 3 do not show an improvement in the performance of the prepared materials. In fact, it is observed that the efficiency of the materials declines when ultrasonic energy is applied during their preparation. This result is attributed to a fusion of the Ca particles when they collide during the application of ultrasonic energy. One of the theories of the particle fragmentation during ultrasonic energy application explains that particles in the slurry are accelerated, and when a collision occurs, they break. Nevertheless, in soft materials, which would be the case of $Ca(OH)_2$, when the collision happens, the particles are fused, so the particle size increases, and in the case of the present work, would diminish the available active size for the SO_2 sorption process.

3.6. Kinetics parameter estimation

Several models have been developed to represent the heterogeneous non-catalytic solid-gas reaction; however, the most popular used to describe the sulfation of solid sorbents are based on the shrinking core process [28-33]. In this model, it is considered that a first-order chemical reaction between the SO_2 and the calcium core of a spherical particle happens first in the outside surface of the particle forming $CaSO_3$/$CaSO_4$. Then, the reaction zone is moved inside the sorbent, leaving behind a converted material and inert solid called “ash” that gradually expands blocking and plugging

the pores of the sorbent material because the molar volume of $CaSO_3$/$CaSO_4$ is higher than that of CaO or $Ca(OH)_2$. In this way, there is an inert layer shrinking during the chemical reaction. The relationship between the time and the covered fraction depends on the rate-limiting step. In order for the reaction to proceed, the SO_2 has to diffuse into the new layer, and it has been shown that rate-limiting step for sulfur uptake is the diffusion of SO_2 through the pores of the new product layer on the particle surface [34]. Therefore, the kinetics model that represents the SO_2 sorption process is

$$\frac{t}{k} = \left[3 - 3(1-\theta)^{2/3} - 2(1-\theta)\right]$$

$$k = \frac{\rho_B \cdot R^2}{6 \cdot b \cdot \mathcal{D}_e \cdot C_g}$$

Where: θ is the covered fraction, ρ_B is the molar density of the active sites in the solid, b is the molar ratio of solid reactant to gas reactant (ratio of stoichiometric coefficient), R is the radius of unreacted core, k is the kinetics constant for the surface reaction, C_g is the SO_2 concentration in the flue gas, $\mathcal{D}_e$ is the effective diffusion coefficient of SO_2 through the "ash".

To improve the adjustment, it was assumed that the SO_2 effective diffusion coefficient, $\mathcal{D}_e$, depends on the conversion since the new product layer modifies the SO_2 diffusion characteristics through the sorbent material:

$$\mathcal{D}_e = \mathcal{D}_{e0} \cdot \left[1 + \alpha_1 e^{(-\alpha_2 \cdot \theta)}\right]$$

Non-linear regression analysis was performed using Polymath™ to determine the kinetics parameters and the results are shown in Tables 2 and 3. According to these results, a good fit was obtained since the R^2_{adj} was high, and with a few exceptions, it was greater than 0.99. Fig. 5 and 6 present the fit between the experimental data and the proposed model.

Table 2. Kinetics parameters for the SO_2 sorption process in the sorbent materials supported on tonsil.

Material	T [°C]	k [min^{-1}]	α_1	α_2	R^2_{adj}
Ca-Tonsil 1:2 MS	350	20030	4.304	-13.794	0.9958
	400	7857.592	4.717	-7.582	0.9993
	450	3557.349	11.494	3.899	0.9990
Ca-Tonsil 1:2 UE	350	93860	15.690	49.632	0.9772
	400	25030	22.191	24.597	0.9937
	450	10100	35.430	28.270	0.9897
Ca-Tonsil 1:1 MS	350	10360	6.403	-6.203	0.9982
	400	410.751	1.917	-17.643	0.9981
	450	183.535	0.521	-17.957	0.9983
Ca-Tonsil 1:1 UE	350	33790	7.029	-17.333	0.9938
	400	29330	6.512	8.704	0.9992
	450	11630	8.030	1.545	0.9984
Ca-Tonsil 2:1 MS	350	20320	0.167	-69.655	0.9950
	400	1096.550	4.715×10^{-6}	-56.786	0.9971
	450	637.864	1.357×10^{-8}	-59.974	0.9930
Ca-Tonsil 2:1 UE	350	8256.339	0.073	-52.494	0.9967
	400	2336.802	0.001	-41.779	0.9996
	450	788.094	2.927×10^{-5}	-39.500	0.9694

Table 3. Kinetics parameters for the SO_2 sorption process in the sorbent materials supported on bentonite.

Material	T [°C]	k [min^{-1}]	A_1	α_2	R^2_{adj}
Ca-Bentonite 1:2 MS	350	118000	5.989	12.577	0.9961
	400	43120	13.700	28.002	0.9986
	450	17260	7.5045	16.996	0.9990
Ca-Bentonite 1:2 UE	350	159400	5.243	52.851	0.9958
	400	39910	7.447	19.008	0.9992
	450	14130	11.815	17.397	0.9995
Ca-Bentonite 1:1 MS	350	1978.496	22.534	-10.788	0.9987
	400	170.806	2.150	-20.357	0.9980
	450	89.447	2.234	-16.238	0.9977
Ca-Bentonite 1:1 UE	350	3207.537	8.1381	-25.955	0.9960
	400	231.918	3.984	-25.851	0.9973
	450	114.568	2.374	-26.532	0.9984
Ca-Bentonite 2:1 MS	350	12890	0.028	-85.340	0.9975
	400	1549.378	1.818×10^{-5}	-54.394	0.9965
	450	542.590	2.99×10^{-6}	-41.960	0.9946
Ca-Bentonite 2:1 UE	350	8784.110	0.037	-65.092	0.9982
	400	1075.256	7.904×10^{-5}	-46.198	0.9985
	450	666.017	1.171×10^{-6}	-50.314	0.9956

To determine the dependency of the diffusion coefficient, $\mathcal{D}_{e0}$, with respect to temperature, it is necessary to point out that it cannot be directly determined because ρ_B and R, which are other physical parameters involved in k, were not experimentally determined. However, some trends with respect to temperature, support, and preparation method are detected. First, it is critically important to emphasize that if the numerical value of k decreases, it implies that $\mathcal{D}_{e0}$ increases since the other parameters are constant, and vice versa, an increase of k means a reduction in the diffusion coefficient. It is observed that in all the prepared materials (regardless the support, Ca load, or preparation method) as temperature increases the value of $\mathcal{D}_{e0}$ also raises. So, an Arrhenius-type dependence with respect to temperature can be obtained. Activation energy was calculated and is presented in Tables 4 and 5. At low Ca loads the activation energy of material supported on tonsil is smaller compared to those supported on bentonite; however, when increasing the Ca load, the activation energy of material supported on bentonite is less when ultrasonic energy is applied during preparation method. This confirms the previous statement that materials supported on bentonite give better results as the Ca load and temperature augments.

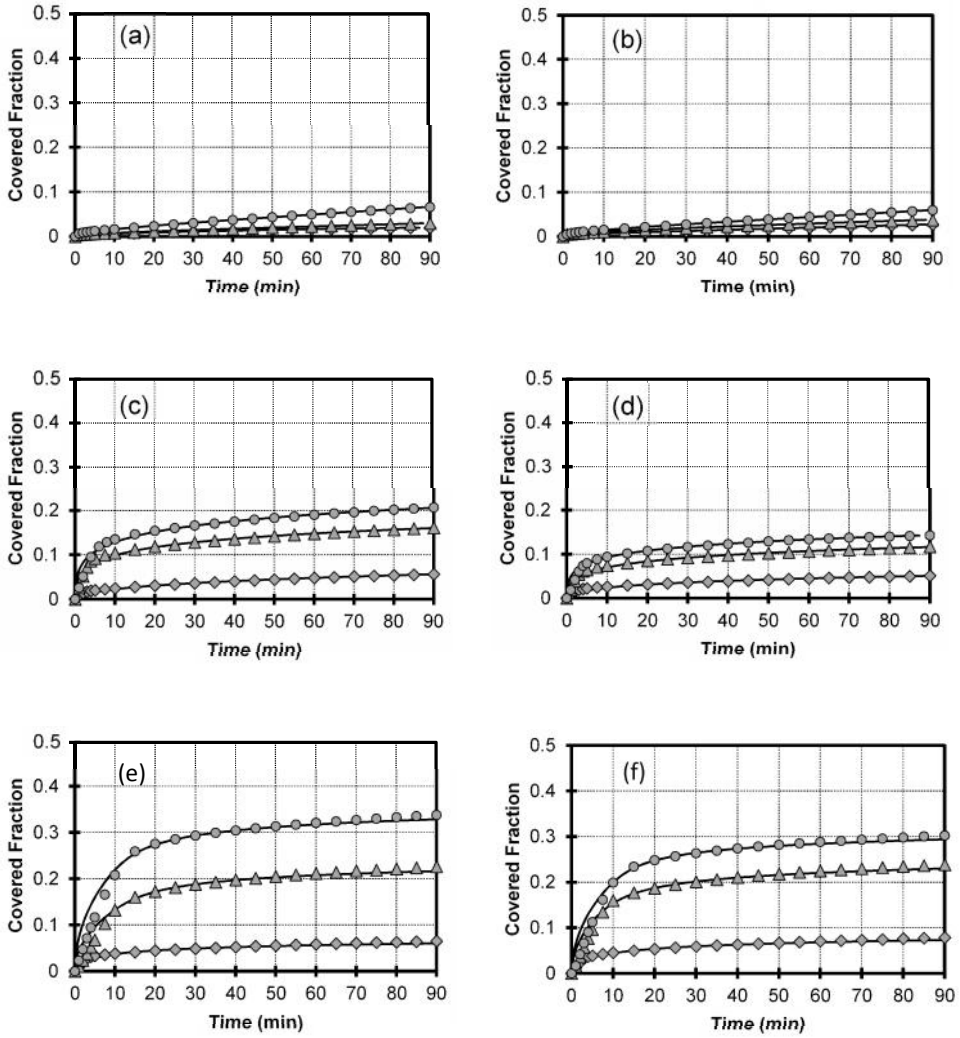

Fig. 5. Adjustment of the experimental data to the kinetics proposed model for $Ca(OH)_2$ supported on bentonite: ◆350°C, ▲ 400°C, ● 450°C. (a) MS 1:2; (b) UE 1:2; (c) MS 1:1; (d) UE 1:1; (e) MS 2:1; (f) UE 2:1

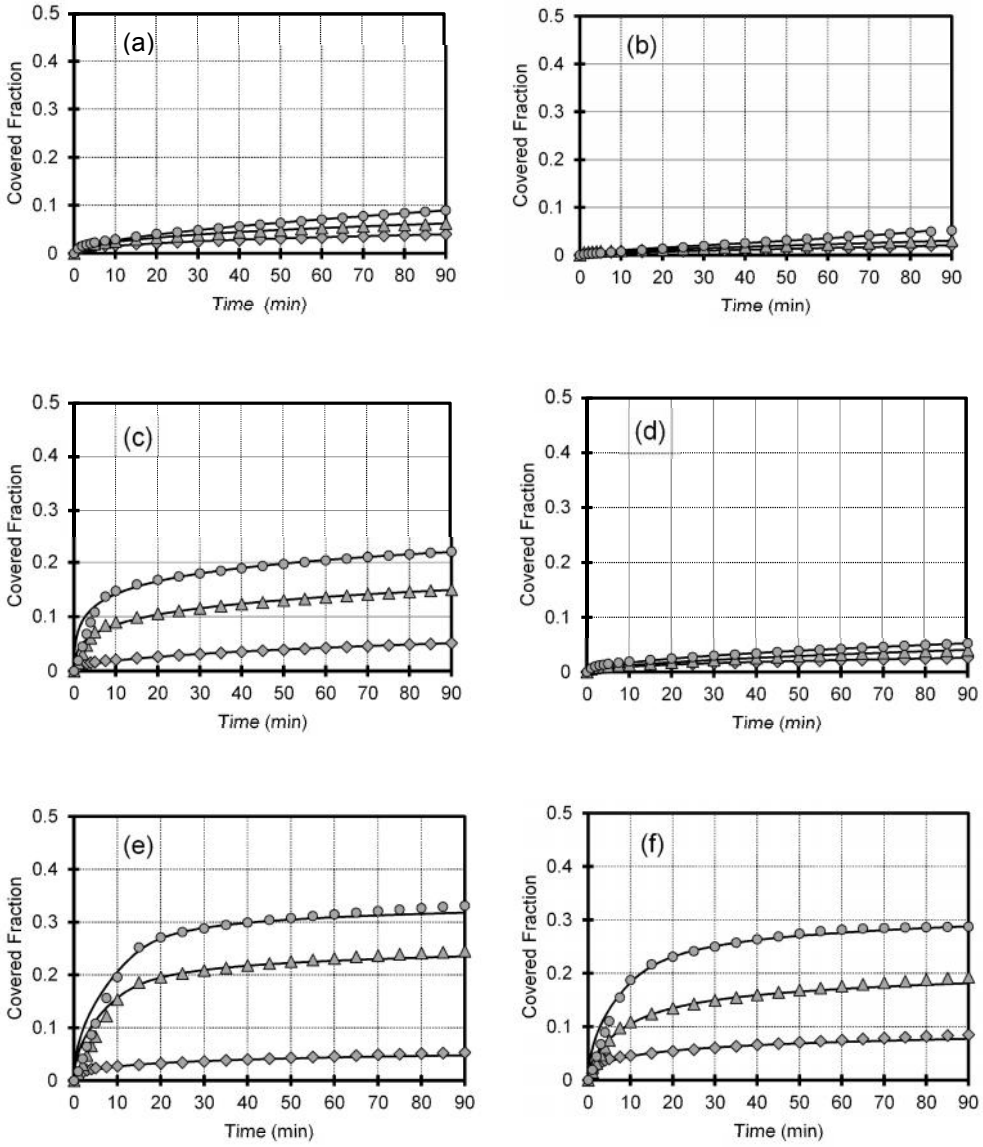

Fig. 6. Adjustment of the experimental data to the kinetics proposed model for $Ca(OH)_2$ supported on tonsil: ◆350°C, ▲ 400°C, ● 450°C. (a) MS 1:2; (b) UE 1:2; (c) MS 1:1; (d) UE 1:1; (e) MS 2:1; (f) UE 2:1

Table 4. Activation energy for the SO_2 sorption process in materials supported on tonsil.

Material	E_A/R [K^{-1}]
Ca-Tonsil 1:2 MS	7,789.5 ± 492.31
Ca-Tonsil 1:2 UE	10,070.0 ± 8,203.81
Ca-Tonsil 1:1 MS	18,410.0 ± 7,004.00
Ca-Tonsil 1:1 UE	4,710.2 ± 2,847.00
Ca-Tonsil 2:1 MS	15,830.0 ± 6,998.00
Ca-Tonsil 2:1 UE	10,590.0 ± 26.07

Table 5. Activation energy for the SO_2 sorption process in materials supported on bentonite.

Material	E_A/R [K^{-1}]
Ca-Bentonite 1:2 MS	8,656.7 ± 1,705.43
Ca-Bentonite 1:2 UE	10,940.0 ± 5,493.74
Ca-Bentonite 1:1 MS	14,130.0 ± 5,190.00
Ca-Bentonite 1:1 UE	15,200.0 ± 5,525.00
Ca-Bentonite 2:1 MS	14,370.0 ± 2,752.00
Ca-Bentonite 2:1 UE	11,780.0 ± 4,718.00

4. CONCLUSION

Materials based on $Ca(OH)_2$ and supported on bentonite and tonsil were prepared at different mass ratios and tested in a thermogravimetric balance to determine their SO_2 sorption capacity. These materials were active for the desulfurization of flue gases, and their activity was improved as the calcium load and temperature increased. On the other hand, support was not important since the activity was almost the same at different experimental conditions; however, at low temperature activity was slightly better for materials supported on tonsil, but those supported on bentonite gave better results as the Ca load and temperature increased. When ultrasonic energy was applied during the preparation of the sorbent materials, their activity decreased, and it was attributed to an agglomeration of Ca particles, so the available active sites decreased. The SO_2 sorption process was represented by a modified shrinking core process model, and the kinetics parameters were estimated using Polymath^{TM}. It was found that the effective diffusion coefficient increased with temperature. Activation energy of materials supported on bentonite was greater at low Ca load, but as this load increased, their activation energy was smaller compared to materials supported on tonsil.

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