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

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ABSTRACT

Aim: The aim of the present work is to develop alternative materials for the flue gas desulfurization process starting from local low-cost raw material in order to reduce the operating cost in a power plant. For this reason, bentonite and tonsil were used as a support, and $\text{Ca}(\text{OH})_2$ as active phase since they are abundant in Mexico.

Study design: Materials were prepared by two different methods and with three different mass ratio Ca: clay. After preparation, materials were tested at three different temperatures in a thermogravimetric balance.

Place and Duration of Study: Samples were prepared at the Universidad Autónoma del Estado de Morelos, and thermogravimetric analysis were made at the Instituto Nacional de Electricidad y Energías Limpias.

Methodology: Materials were prepared with slurries of different Ca: clay mass ratio (1:2, 1:1, and 2:1) using mechanical stirring or applying ultrasonic energy during mixing. To quantify the real calcium content, samples were dissolved and analysed by Atomic Absorption Spectroscopy. Materials were tested at 350, 400, and 450°C in a thermogravimetric balance to determine their sorption capacity. The process was modelled using a modified shrinking core approach, and kinetic parameters were estimated.

Results: It was found that activity increased proportionally to the Ca load and temperature. Clays did not play a significant role; at low heat, an action was slightly better in materials supported on tonsil, but at higher temperatures, elements supported on bentonite had better activity. Ultrasonic energy did not improve the performance of sorbent materials. The modified shrinking core model adequately fit the experimental data.

Conclusions: Sorbent materials prepared in this study were able to retain SO_2 at the studied temperatures, and are an economical alternative for the flue gas desulfurization process. Ca load was the most relevant parameter for the physical activity.

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14 *Keywords: acid rain, $\text{Ca}(\text{OH})_2$, tonsil, bentonite, sorbent materials, flue gas desulfurization,*
15 *ultrasonic energy, kinetics parameter estimation*

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1. INTRODUCTION

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20 The combustion of fossil fuel for the generation and transformation of energy in sectors,
21 such as industry, transport and commercial has caused an increase in the concentrations of
22 gaseous and particulate pollutants in the atmosphere. This increase in contaminants has
23 resulted in air pollution. One of the most critical environmental problems is the acid rain,
24 which is a broad term that describes several ways through which acid falls out, including
25 acidic rain, fog, hail and snow. At the beginning of the problem, acidic rainfall was commonly
26 detected around industrial areas; however, with the increased use of tall stacks for power
27 plants and industries, atmospheric emissions are now transported beyond the industrial

28 areas. Acid rain is the result of many steps of chemical reactions between airborne
29 pollutants (oxides of sulfur, nitrogen and other constituents present in the atmosphere) and
30 atmospheric water and oxygen. Primary sources of these oxides are fossil fuel-fired power
31 stations and smelters for SO_2 , and motor vehicle exhausts for NO_x . These oxides may react
32 with other chemicals and produce corrosive substances that are washed out either in wet or
33 dry form by rain as acid deposition [1-3].

34 Acid rain has several effects on the ecosystem, which include the decay in the growth of
35 trees, crops, aquatic flora and fauna. Besides, soil fertility is deteriorated as a result of
36 leaching of nutrient cations and the increased availability of toxic heavy metals. Also, stones,
37 metals, paints, textiles and ceramics can be eroded and corroded due to acid rain. It can
38 also indirectly affect human health since it has been shown that SO_2 and NO_x contribute to
39 the formation of $\text{PM}_{2.5}$ [3-6]. The acid rain problem has been tackled to some extent in
40 developed countries by reducing the emission of the precursor gases, and several actions
41 have been created in different parts of the world i.e., the Gothenburg Protocol for the
42 European Union and the US Acid Rain Program in the Title IV of the 1990 Clean Air Act
43 Amendments. [7-10].

44 Due to the rapid economic development and energy consumption throughout the world,
45 fossil fuel consumption has significantly increased during the last few decades. The use of
46 fossil fuel is the primary cause of large-scale generation of acid precursors in the
47 atmosphere. The problem was initially identified as an issue in developed countries, but with
48 the increase in industrialisation and urbanisation, developing countries are now also
49 experiencing this issue.

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

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67 **2. MATERIAL AND METHODS**

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69 **2.1. Sorbent Preparation**

70 Samples of $\text{Ca}(\text{OH})_2$ supported in bentonite and tonsil were synthesised by preparing
71 slurries at the different mass ratio. Some of them were mechanically stirred during four h at
72 60-70°C. In other muds, ultrasonic energy was applied during four h maintaining the
73 temperature below 70°C. After the mixing, slurries were dried overnight a 120°C and
74 pulverised.

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76 **2.2. Sorbent characterisation**

77 To determine the actual calcium content, samples of the sorbent-materials were dissolved
78 and analysed by Atomic Absorption Spectroscopy. Table 1 presents the composition of the
79 different materials.

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84 **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

85 MS: Mechanical Stirring

86 UE: Ultrasonic Energy

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89 **2.3. Sulfation of sorbents**

90 The sulfation of the materials was carried out in a thermogravimetric balance (TA
 91 Instruments 2050) by passing a stream of certified 3600 ppm_v SO₂/N₂ through a known
 92 amount of sorbent material. The gas flow rate was 100 mL/min, which is the maximum flow
 93 of the thermobalance. The gain of weight in the article was assigned to the sorption of SO₂
 94 on the active sites. To ensure reproducibility of the results, the analyser is monthly calibrated
 95 according to international standards by a certified agency.

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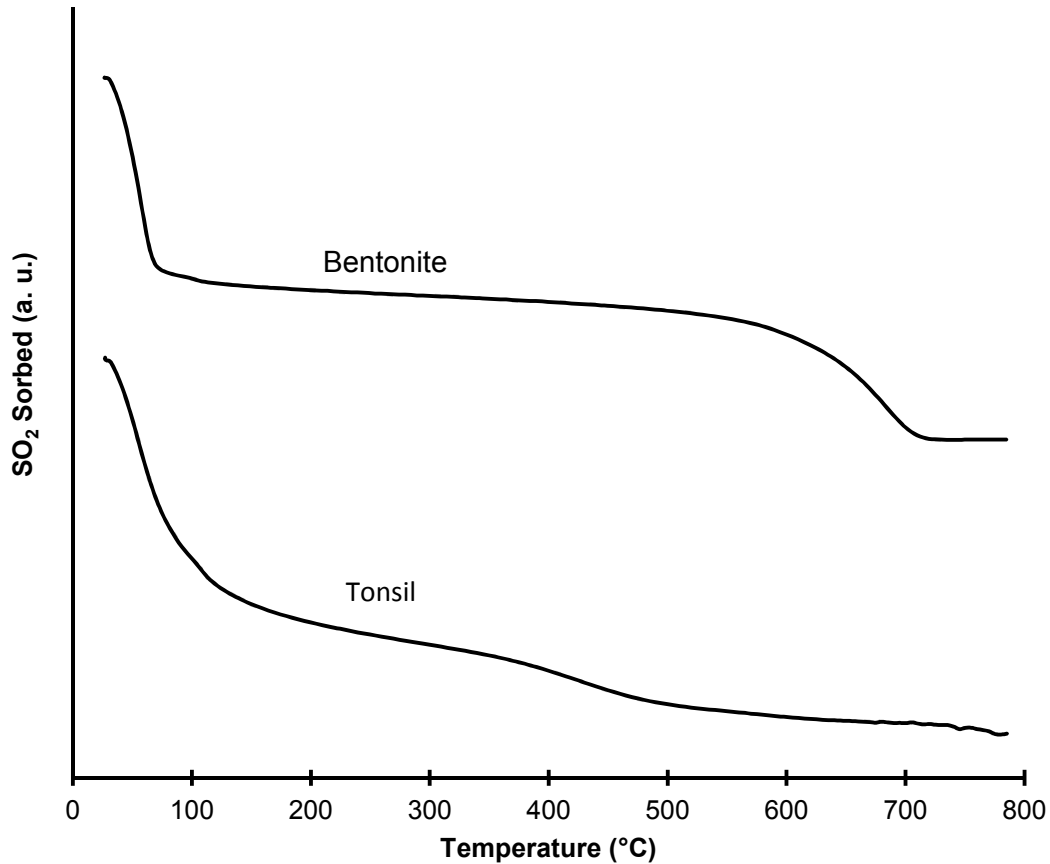
98 **3. RESULTS AND DISCUSSION**

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100 **3.1. Sorption of SO₂ on bentonite and tonsil**

101 Experiments in the TGA different temperature (heating rate: 10°C/min) were performed to
 102 check if supports were able to adsorb SO₂. Results are presented in Fig. 1, and it was
 103 observed that none of the clays retained SO₂. In fact, it was noticed that weight loss
 104 occurred as the temperature increased; however, this is attributed to a loss of humidity in the
 105 interval between room temperature and 120°C. Then, a drastic weight loss was observed,
 106 especially in bentonite, at temperatures higher than 550°C; this is a result of the thermal
 107 rearrangement of the crystalline structure.

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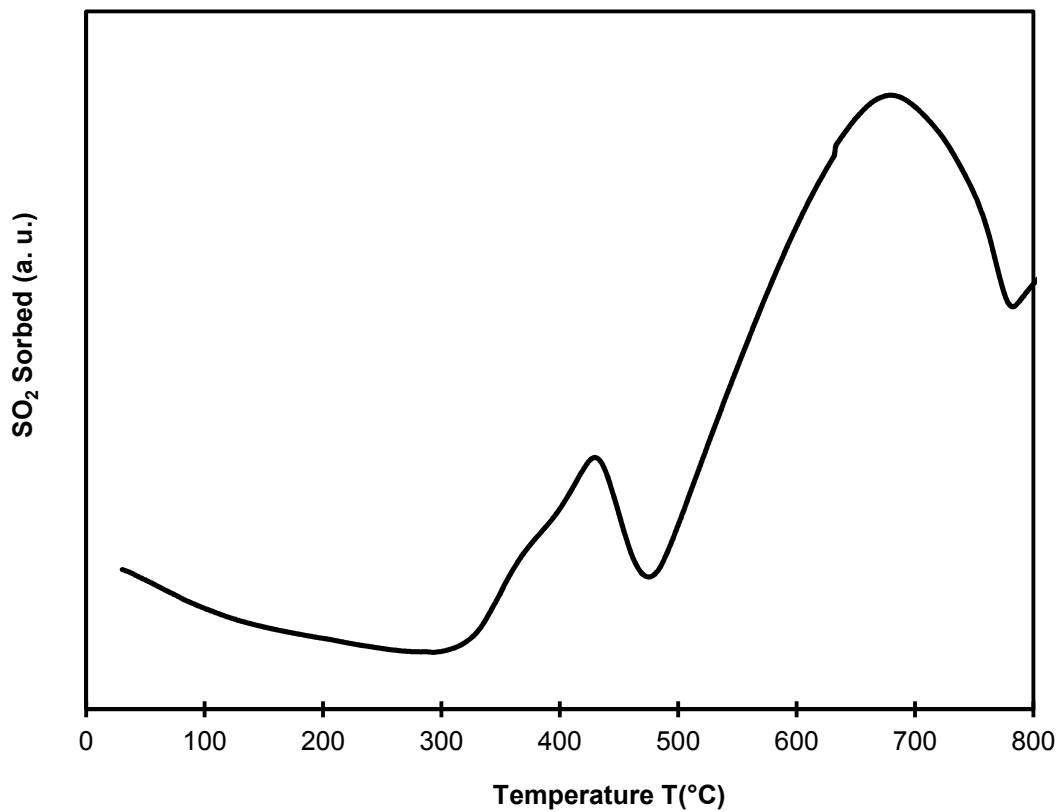


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Figure 1. Thermogravimetric profiles of the supports in the sulfurization process at variable temperature.

3.2. Effect of temperature in the sorption capacity

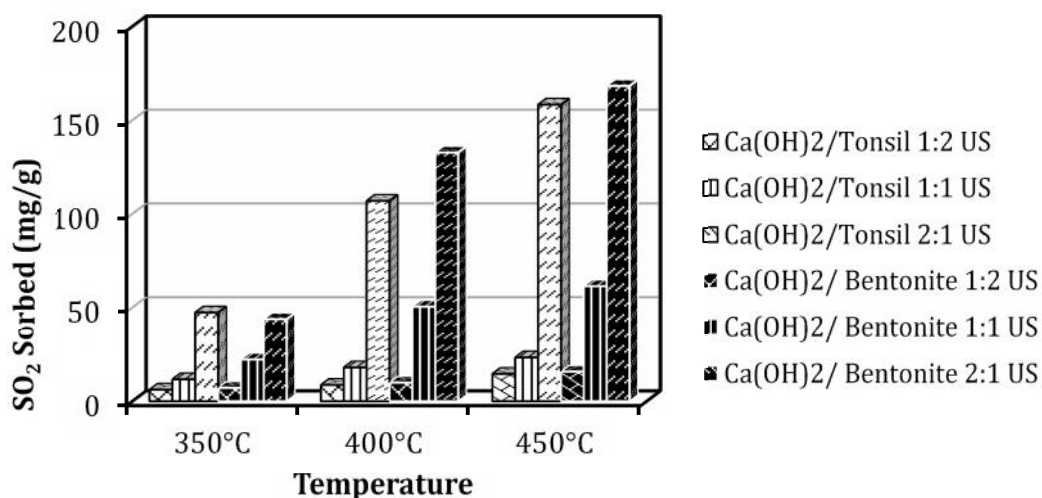
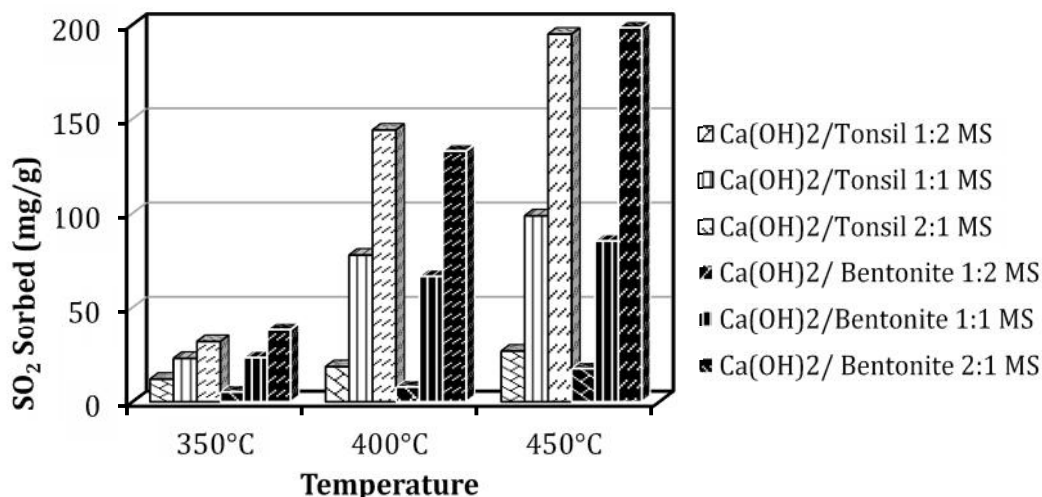
To determine the temperature interval in which the sorbents were studied, an experiment in the TGA with pure Ca(OH)₂ at a heating rate of 10°C/min was performed. The result is shown in Fig. 2. It is observed that the SO₂ sorption process begins at 300°C, and it continues up to 650°C. At temperature interval of 420-480°C has 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 SO₂. 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.



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

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

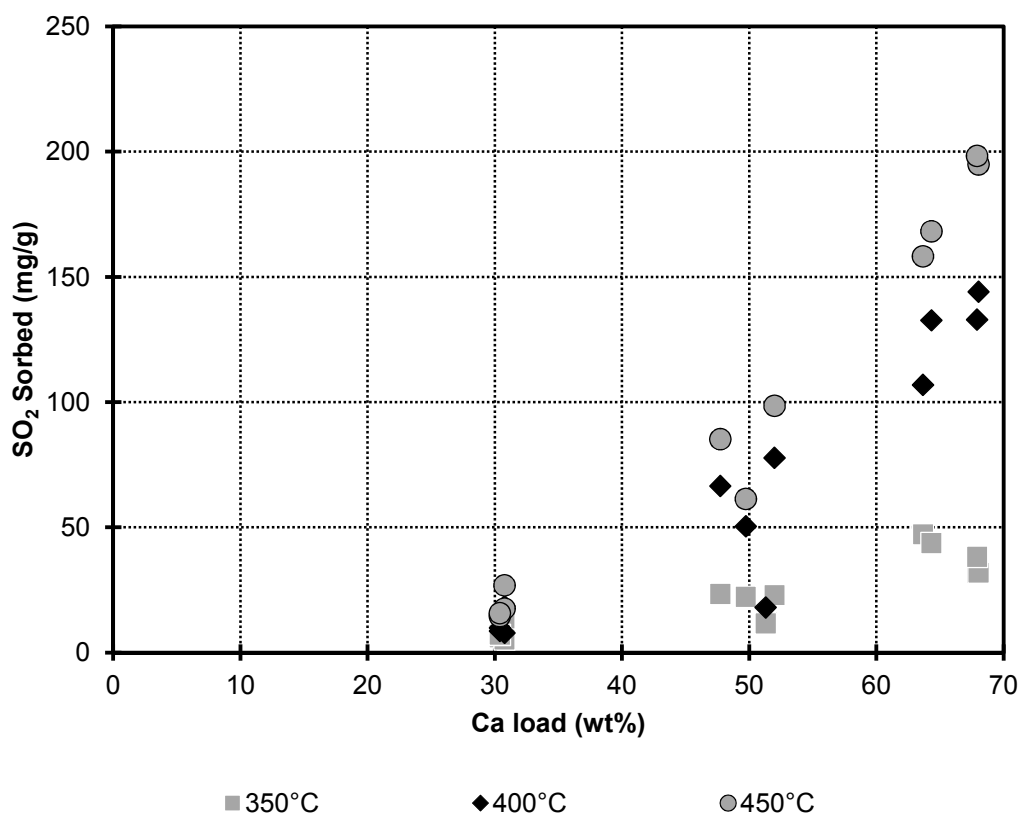


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Fig. 3. The SO₂ sorption capacity of the different prepared materials at 90 min.

3.3. Effect of calcium load

According to the results presented in Fig. 4, Ca load plays a vital 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 to 98 mg/g, which is 3.6 times more than at 31 wt %. Moreover, when Ca load is 68 wt% (1.3 times concerning the last charge), the sorption capacity increases two times compared to the previous amount, 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].



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153 **Fig. 4. Effect of calcium load in the SO₂ sorption capacity of the prepared materials.**
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156 **3.4. Effect of support**

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

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163 **3.5. Effect of preparation method**

164 Ultrasonic energy was used trying to improve the yield of the proposed materials. Since the
165 application of high elements in slurries can fragment the solid particles, decreasing their
166 size, it is intended that this event would multiply the number of available active sites for the
167 SO₂ sorption process. Nevertheless, the results presented in Fig. Three do not show an
168 improvement in the performance of the prepared materials. In fact, it is observed that the
169 efficiency of the materials declines when ultrasonic energy is applied during their
170 preparation. This result is attributed to a fusion of the Ca particles when they collide during
171 the application of ultrasonic energy. One of the theories of the particle fragmentation during
172 ultrasonic energy application explains that particles in the slurry are accelerated, and when a
173 collision occurs, they break. Nevertheless, in soft materials, which would be the case of
174 Ca(OH)₂, when the accident happens, the particles are fused, so the particle size increases,
175 and in the fact of the present work, would diminish the available active size for the SO₂
176 sorption process.

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3.6. Kinetics parameter estimation

Several models have been developed to represent the different 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 SO₂ and the calcium core of a spherical particle happens first in the outside surface of the particle forming CaSO₃/CaSO₄. 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 CaSO₃/CaSO₄ 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. For the reaction to proceed, the SO₂ has to diffuse into the new layer, and it has been shown that rate-limiting step for sulfur uptake is the diffusion of SO₂ through the pores of the new product layer on the particle surface [34]. Therefore, the kinetics model that represents the SO₂ sorption process is given in Equation 1 and 2.

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

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

Where: θ is the covered fraction, ρ_B is the molar density of the active sites in the stable, 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 kinetic constant for the surface reaction, C_g is the SO₂ concentration in the flue gas, \mathcal{D}_e is the effective diffusion coefficient of SO₂ through the “ash”. To improve the adjustment, it was assumed that the SO₂ effective diffusion coefficient, \mathcal{D}_e , depends on the conversion since the new product layer modifies the SO₂ diffusion characteristics through the sorbent material as is represented in Equation 3.

$$\mathcal{D}_e = \mathcal{D}_{e0} \cdot \left[1 + \alpha_1 e^{(-\alpha_2 \theta)} \right] \quad \text{Equation 3}$$

Non-linear regression analysis was performed using Polymath™ to determine the kinetic 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. It is interesting to notice that α_2 takes negative values depending on the calcium load since materials with relationship 1:1 and 2:1 Ca: support, α_2 is negative. This may be assigned to the Ca species formed during sulfation (CaSO₃ or CaSO₄) and their tendency to modify the \mathcal{D}_e during the process. A negative α_2 indicates that \mathcal{D}_e is not considerably affected by the conversion. Fig. 5 and 6 present the fit between the experimental data and the proposed model.

Table 2. Kinetics parameters for the SO₂ 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

	350	10360	6.403	-6.203	0.9982
Ca-Tonsil 1:1 MS	400	410.751	1.917	-17.643	0.9981
	450	183.535	0.521	-17.957	0.9983
	350	33790	7.029	-17.333	0.9938
Ca-Tonsil 1:1 UE	400	29330	6.512	8.704	0.9992
	450	11630	8.030	1.545	0.9984
	350	20320	0.167	-69.655	0.9950
Ca-Tonsil 2:1 MS	400	1096.550	4.715×10^{-6}	-56.786	0.9971
	450	637.864	1.357×10^{-8}	-59.974	0.9930
	350	8256.339	0.073	-52.494	0.9967
Ca-Tonsil 2:1 UE	400	2336.802	0.001	-41.779	0.9996
	450	788.094	2.927×10^{-5}	-39.500	0.9694

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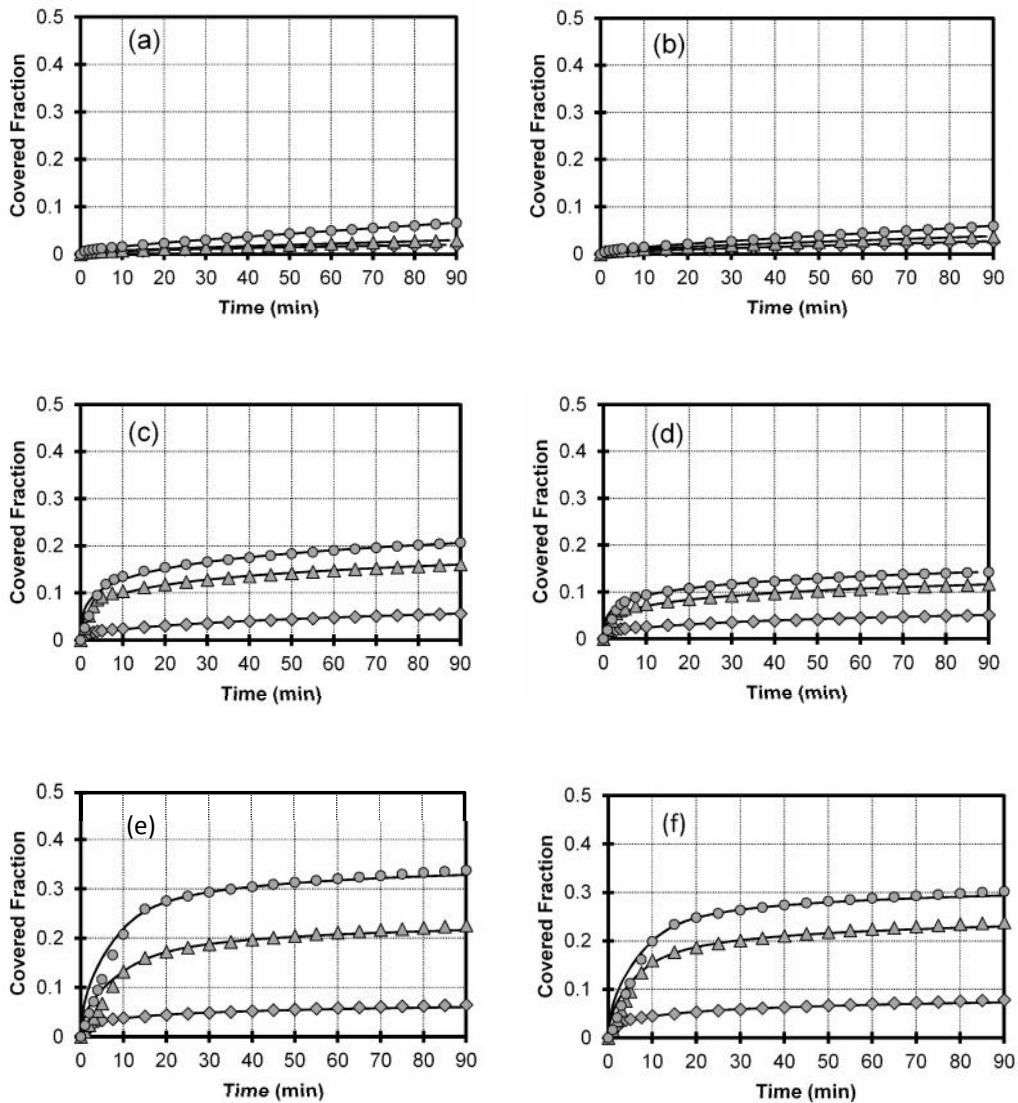
Table 3. Kinetics parameters for the SO₂ sorption process in the sorbent materials supported on bentonite.

Material	T [°C]	k [min ⁻¹]	α_1	α_2	R ² _{adj}
	350	118000	5.989	12.577	0.9961
Ca-Bentonite 1:2 MS	400	43120	13.700	28.002	0.9986
	450	17260	7.5045	16.996	0.9990
	350	159400	5.243	52.851	0.9958
Ca-Bentonite 1:2 UE	400	39910	7.447	19.008	0.9992
	450	14130	11.815	17.397	0.9995
	350	1978.496	22.534	-10.788	0.9987
Ca-Bentonite 1:1 MS	400	170.806	2.150	-20.357	0.9980
	450	89.447	2.234	-16.238	0.9977
	350	3207.537	8.1381	-25.955	0.9960
Ca-Bentonite 1:1 UE	400	231.918	3.984	-25.851	0.9973
	450	114.568	2.374	-26.532	0.9984
	350	12890	0.028	-85.340	0.9975
Ca-Bentonite 2:1 MS	400	1549.378	1.818×10^{-5}	-54.394	0.9965
	450	542.590	2.99×10^{-6}	-41.960	0.9946
	350	8784.110	0.037	-65.092	0.9982
Ca-Bentonite 2:1 UE	400	1075.256	7.904×10^{-5}	-46.198	0.9985
	450	666.017	1.171×10^{-6}	-50.314	0.9956

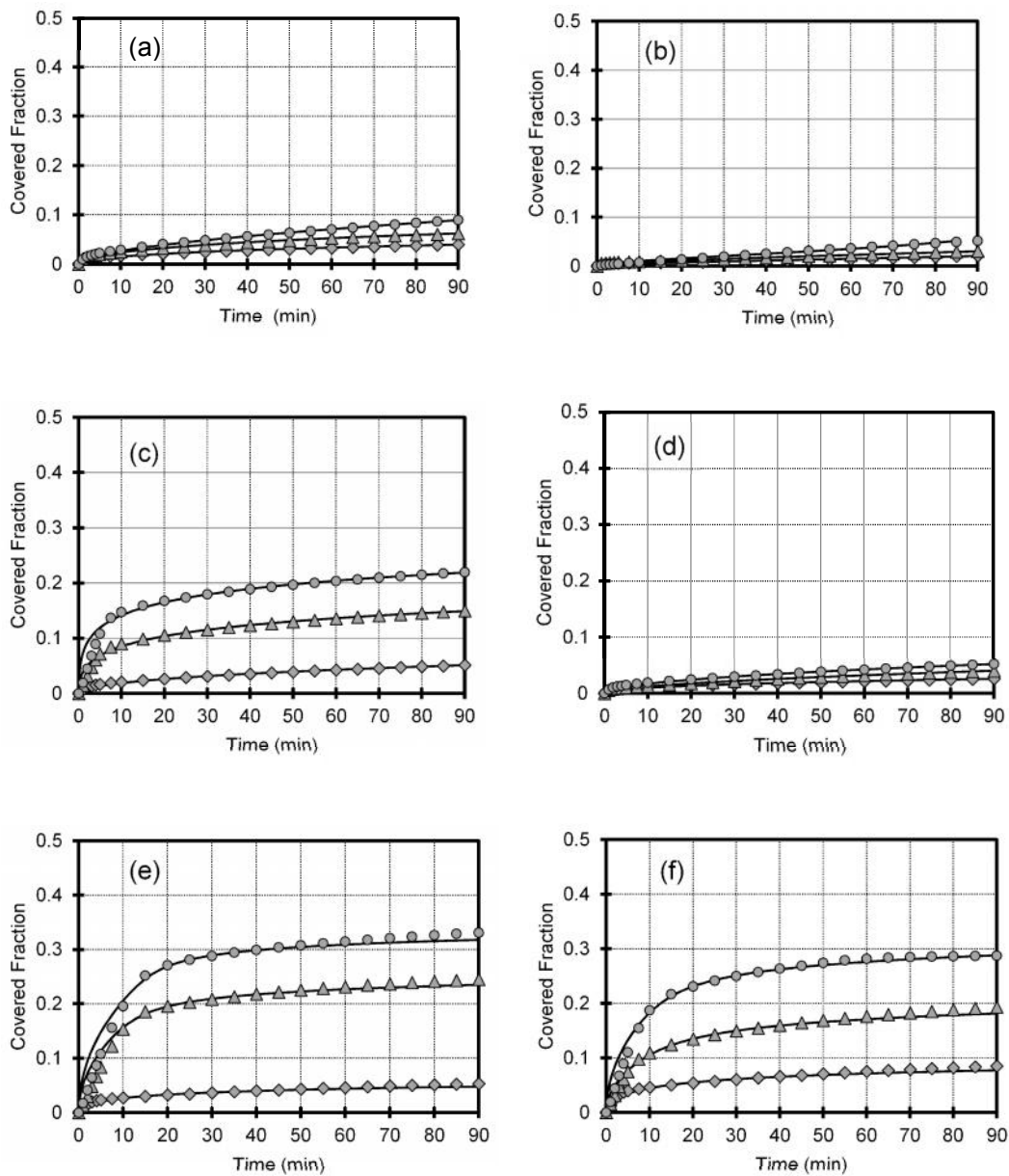
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To determine the dependency of the diffusion coefficient, \mathcal{D}_{e0} , concerning temperature, it is necessary to point out that it cannot be directly determined because R_B and R , which are other physical parameters involved in k , were not experimentally determined. However, some trends concerning temperature, support, and preparation method are detected. First, it is critically important to emphasise that if the numerical value of k decreases, it implies that \mathcal{D}_{e0}

229 increases since the other parameters are constant, and vice versa, an increase of k means a
 230 reduction in the diffusion coefficient. It is observed that in all the prepared materials
 231 (regardless the support, Ca load, or preparation method) as temperature increases the value
 232 of D_{e0} also raises. So, an Arrhenius-type dependence concerning temperature can be
 233 obtained. The activation energy was calculated and is presented in Tables 4 and 5. In some
 234 cases, confidence limits are quite high, but they are still statistically acceptable. These
 235 variations may be attributed to the Ca species that are formed during the reaction. At low Ca
 236 loads the activation energy of material supported on tonsil is smaller compared to those
 237 recommended on bentonite; however, when increasing the Ca load, the activation energy of
 238 material supported on bentonite is less when ultrasonic energy is applied during preparation
 239 method. This confirms the previous statement that elements supported on bentonite give
 240 better results as the Ca load and temperature augments.
 241



243 **Fig. 5. Adjustment of the experimental data to the kinetics proposed model for**
244 **Ca(OH)₂ supported on bentonite: ◆ 350°C, ▲ 400°C, ● 450°C. (a) MS 1:2; (b) UE 1:2; (c)**
245 **MS 1:1; (d) UE 1:1; (e) MS 2:1; (f) UE 2:1**
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Fig. 6. Adjustment of the experimental data to the kinetics proposed model for Ca(OH)_2 supported on tonsil: \blacklozenge 350°C, \blacktriangle 400°C, \bullet 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

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Table 4. The activation energy for the SO₂ 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

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Table 5. The activation energy for the SO₂ 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

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4. CONCLUSION

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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 SO₂ 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 crucial since the movement 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. A modified shrinking core process model represented the SO₂ sorption process, and the kinetic parameters were estimated using PolymathTM. It was found that the effective diffusion coefficient increased with temperature. The activation energy of materials supported on bentonite was more significant at low Ca load, but as this load increased, their activation energy was smaller compared to elements supported on tonsil.

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