CHARACTERIZATION AND BEHAVIOUR OF MODIFIED CALCIUM HYDROXIDE BASED SORBENTS IN A DRY DESULFURIZATION PROCESS

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Abstract

Several calcium hydroxide based sorbents were prepared by hydration of commercial $Ca(OH)_2$ and a magnesic smectite using two lignosulfonates as additives, and their structural and desulfurant properties were studied. The sorbents were characterized by using scanning electron microscopy (SEM) with an X-Ray detector and N_2 adsorption techniques. The dry desulfurization activity at low temperature was investigated in a laboratory scale equipment. When LGS are used in low amounts, their dispersant or deagglomerating properties observed by SEM produce an increase in the porosity and in the specific surface area (SSA) respect to the sorbent prepared without LGS. Their desulfurization activity increases up to 71% respect to the solid prepared without additive, being the increase in the porosity and in the SSA values the main factor to explain the higher SO_2 retention values, but also their hygroscopic properties. The composition of the spent sorbents allows to use them as soil amendment. The use of these LGS in the preparation of calcium based sorbents is an excellent and easy way to improve their desulfurant behavior, with an easy preparation at ambient temperature, and it is also another promising option to valorize this lignocellulosic waste.

Keyword: Lignosulfonates, Smectite, $Ca(OH)_2$, Particle Properties, Desulfurization.

1. INTRODUCTION

Coal fired power plants provide about 10.2 % of the energy requirements in Spain[1]. These plants are one of the most relevant sources of air pollutants as SO_x, NO_x or particulate matter. The Directive (2010/75/EU)[2], states more restrictive SO_2 emission limit values for these combustion plants. These environmental regulations promote the development of more efficient uses of coal in processes as oxycombustion, co-combustion, integrated gasification combined cycle (IGCC) or the use of more efficient desulfurization sorbents. To enhance the reactivity of commercial calcium or magnesium based sorbents, different options that basically produce solids with higher SSA have been tried[3-6].

The use of additives, as hygroscopic salts[7] or surfactants, for improving sorbents utilization has also frequently been investigated. Lignosulphonates, salts of lignosulfonic acid formed when wood pulp is manufactured by the sulphite method, are produced in our region of Cantabria (Spain) by Lignotech Ibérica. Although burning to produce process steam, is still the main use of these products, advances in lignin technology have led to the development of products that, with or without modification, may be used as surfactants, binders, dispersants, emulsifiers in animal feed, concrete or ceramics additives, complexing agents, mining aids, etc.[8-11]. To valorize LGS within the biorefinery framework, the production of vanillin or other phenolic aldehydes and its utilization after modification in the formulation of phenol formaldehyde resins[12-14] is also promoted.

LGS have also been used as additives in the preparation of desulfurant particles and the positive effect of these additives has been reported[15-20].

Sorbents prepared by mixing different clays and CaO or $Ca(OH)_2$ at room temperature, are a good alternative to conventional sorbents in dry or semidry desulfurization processes at low temperature due to the easy and cheap process of preparation and to the good results found capturing SO_2 [21,22]. In previous works[5,23] this type of sorbents were prepared, characterized and used to retain SO_2. The best results were obtained with sorbents prepared by wet mixture, at room temperature, of the calcium base and the clay smectite at a 1/10 calcium base/smectite ratio. Considering that previous results, the scope of this work was to evaluate the effectiveness of LGS in the structural and desulfurant properties of sorbents prepared by mixing calcium hydroxide and smectite at room temperature.

2. MATERIALS AND METHODS

2.1. Materials. Calcium Hydroxide of commercial quality, with a 83% of $Ca(OH)_2$, 9% of $CaCO_3$ and a SSA of 16.2 m^2/g was supplied by Calcinor, S.A, Altzo/Guipúzcoa, Spain. The clay magnesium smectite (saponite) was supplied by Tolsa S.A, Madrid, being the SSA value of 165 m^2/g and the particle size less than 60 µm. More detailed physicochemical properties of these raw materials have been previously referred[5]. Two lignosulfonates supplied by Lignotech Ibérica Torrelavega /Cantabria: Borresperse CaI-50, an aqueous solution of calcium lignosulphonate at 50%, free of $CaSO_4$ and sugars and Borresperse NaI-50, an aqueous solution at 50% of sodium lignosulphonate also free of impurities were used as additives.

2.2. Preparation of sorbents. Basing on the best hydration conditions found in previous works[5,23], the procedure involves the addition of 1 g. of $Ca(OH)_2$ to 50 ml of distilled water containing the dissolved LGS in amounts ranging from 0.1 to 0.4 weight % with respect to the total solid (calcium hydroxide and smectite) being the suspension magnetically stirred 15 minutes; after, 10 grams of smectite were added and the mixture was again stirred 30 minutes at room temperature. The dense slurry, without filtering, was dried in an oven at 60ºC until constant weight, usually for 24 hours. A sorbent (S9) was prepared at the same conditions without LGS. Table 1 shows the composition of the sorbents.

2.3. Characterization. The specific surface area (SSA) of the sorbents was calculated using the B.E.T. method from N_2 adsorption data. The experiments were performed in a Micromeritics ASAP-2010 apparatus. The pore size distribution of S1 and S9 was obtained from N_2 adsorption-desorption experiments according to the BJH method. The morphology of S1, S2 and S9 sorbents, prepared with and without LGS, was studied using a JEOL JSM5800-LV scanning electron microscope (SEM) with an X-Ray Oxford DCL 7849 detector.

Table 1. Chemical composition of the sorbents prepared

Sorbent`s identification	**Composition**
S1	[$Ca(OH)_2$ + Smectite][1/10] +Borresperse NaI-50, 0.1%
S2	[$Ca(OH)_2$ +Smectite][1/10] + Borresperse NaI 50, 0.2%
S3	[$Ca(OH)_2$ + Smectite][1/10] + Borresperse NaI-50, 0.3%
S4	[$Ca(OH)_2$ + Smectite][1/10] + Borresperse NaI-50, 0.4%
S5	[$Ca(OH)_2$ + Smectite][1/10] + Borresperse CaI-50, 0.1%
S6	[$Ca(OH)_2$ + Smectite][1/10] + Borresperse CaI-50, 0.2%
S7	[$Ca(OH)_2$ + Smectite][1/10] + Borresperse CaI-50, 0.3%
S8	[$Ca(OH)_2$ + Smectite][1/10] + Borresperse CaI-50, 0.4%
S9	[$Ca(OH)_2$ + Smectite][1/10] (Blank)

2.4. Desulfurization Activity. The desulfurization activity test was performed in a glass-made jacketed fixed bed reactor, under isothermal conditions at 58°C and a relative humidity of 58%. Approximately 2 g of the sorbent was weighed and dispersed manually in 30 g of an inert sand bed and the whole bed supported on a 3.6 cm diameter fritted glass plate contained in the glass cylinder. The apparatus used in this study is shown in Figure 1, and was described in previous works[3,5,7]. The baths showed in the figure 1 are necessary to maintain the reactor temperature and humidity conditions.

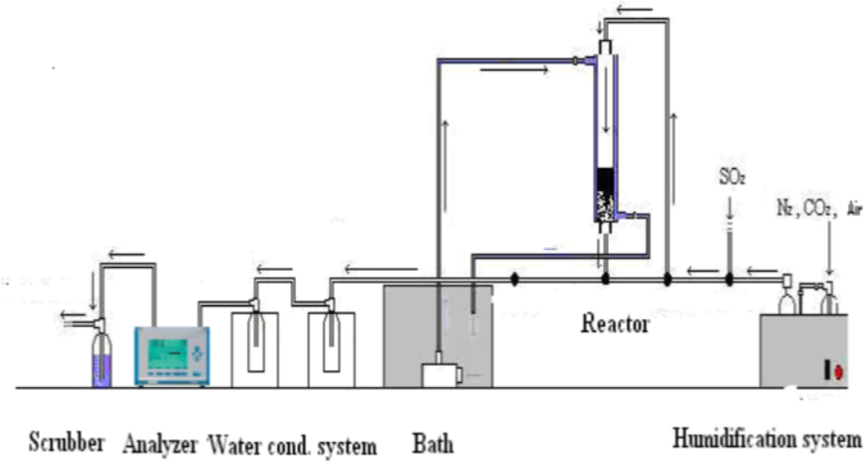


Figure 1. Experimental set up of the reaction process.

The volume composition of the gas was 2500 ppm SO_2, 12% CO_2, 2% O_2 and balance N_2, at a rate of 1000 cm^3/ min. The gas stream without SO_2 passed through the humidification system. After humidification, the gas mixture with SO_2 flowed through the reactor. Two runs were performed with each sorbent. The concentration of SO_2 after the reaction was continuously monitored with an Emerson MLT-1 NGA 2000 gas analyzer and data were compiled with a personal computer equipped with NGA win control software. The reaction time, controlled by the breakthrough curves, was 1 hour approximately. The calcium utilization or the calcium conversion in the desulfurization reaction, in percent, is defined as:

$$\frac{\frac{moles\ of\ SO_2 captured}{grams\ of\ sorbent}}{\frac{moles\ of\ calcium\ in\ the\ sorbent}{grams\ of\ sorbent}} \text{ x 100, (Equation 1)}$$

The moles of SO_2 captured were calculated from the area above the breakthrough curves. The moles of calcium in the sorbent were obtained considering the $Ca(OH)_2$/ smectite ratio, the commercial calcium hydroxide composition and the amount of CaO present in the smectite.

According to a previous work[24] the main desulfurization product, at the experimental conditions is $CaSO_3.1/2H_2O$.

3. RESULTS AND DISCUSSION

3.1. Physicochemical properties of the sorbents. The specific surface area values of calcium hydroxide, of S9 and of all the sorbents are shown in Figure 2.

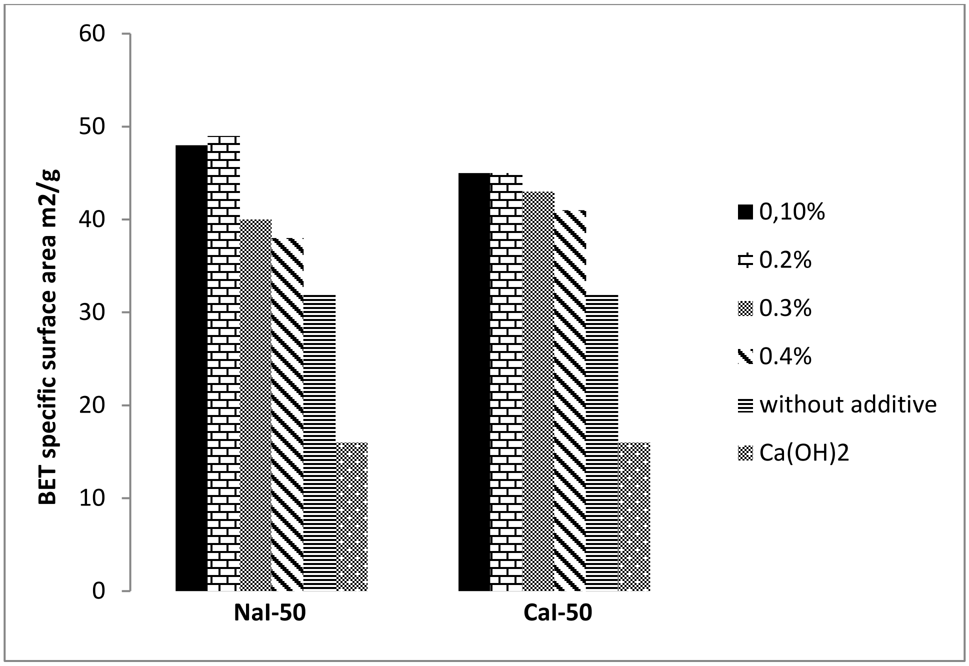


Figure 2. BET specific surface area of the sorbents prepared with both lignosulfonates, of a sorbent prepared without additive and of commercial calcium hydroxide.

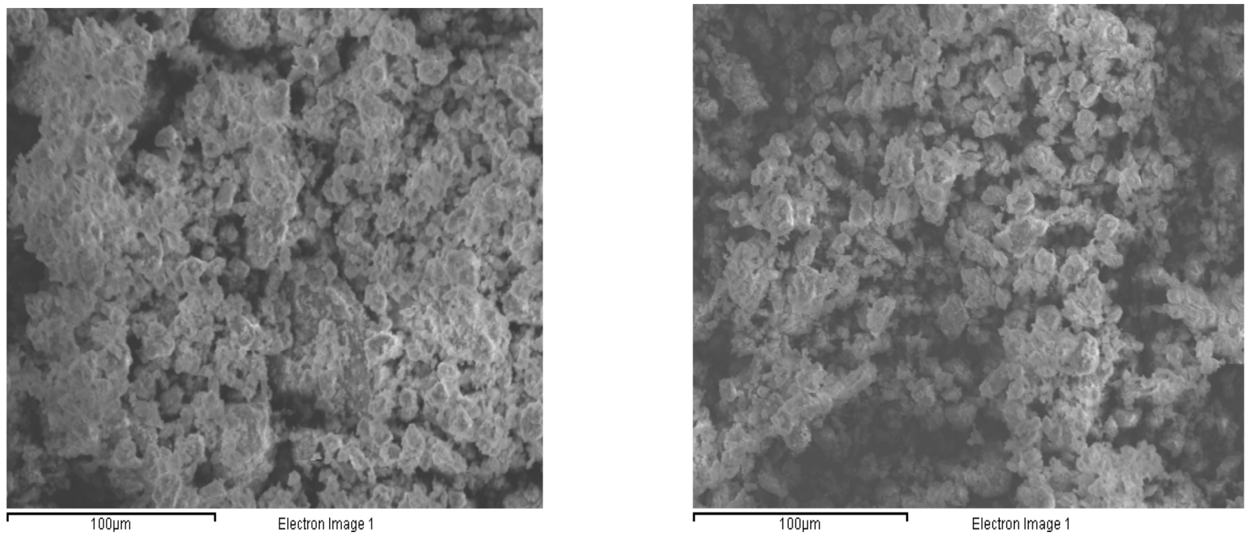
As figure shows, the solid prepared without additive S9, has a surface value of 32 m^2/g much lower than that of 165 m^2/g that corresponds to the support smectite. This drastic reduction was previously explained[5] considering that the calcium hydroxide plugs the entrance to the interlaminar holes of smectite during the hydration process. Sorbents prepared with additives have specific surface area values within 38 and 49 m^2/g, being all of them higher than 32 m^2/g. As Figure 2 shows, the effect on the SSA of the amount of the additive Borresperse CaI-50 is not relevant, in the range of amounts of LGS tested, as values varies from 45 to 41 m^2/g when the amount of additive increases from 0.1 to 0.4 wt %. Figure 2 also shows that the highest surface area values are obtained with the lowest amounts of both additives (0.1 and 0.2%). Table 2 shows the total pore volume, the pore size distribution and the specific surface area of the S1 and S9 solids.

Table 2. BET specific surfacea area, total pore volume, pore size distribution and average pore diameter of sorbent 1, prepared with 0.1% of Borresperse NaI-50 and of sorbent 9 (blank).

Solid	**S1**	**S9 (Blank)**
BET specific surface area (m^2/g)	48	32
Total pore volume (cm^3/g)	0.074	0.066
Micropore volume (cm^3/g)	0.0038	0.0011
Mesopore volume (cm^3/g)	0.067	0.063
Average pore diameter (Å)	63.53	82.82

Data in this table show that the additive decreases the average pore diameter and increases the porosity in the micro (in 0.0027 cm^3/g) and mainly in the mesopore zone (in 0.004 cm^3/g) and this increase is reflected in the SSA value.

Figure 3 shows the SEM images of the S9 and S1 sorbents, prepared without and with LGS respectively.



a) **b)**

Figure 3. SEM images: a) S9, sorbent without LGS and b) S1 sorbent with LGS.

The dispersant or deagglomerating effect of LGS can explain the differences between S9 and S1 images. Sample S1 prepared with LGS exhibit a less agglomerated solid, with a smaller particle size and pore size. These images confirm the measured changes in the specific surface area and porosity values presented in Table 2.

Results of X-Ray detector performed in 5 different places of SEM images of S9, S1 and S2 samples show a uniform calcium distribution on the smectite surface in all the sorbents. Table 3 shows the Ca% mean values for the three solids and the standard deviation found.

Table 3. Calcium percent values obtained with the X-Ray detector on the surface of S9, S1 and S2 sorbents

Sorbent	Mean Ca values (%)
S9 (Blanck)	11±1
S1 (0.1 % LGS)	9±2
S2 (0.2 % LGS)	9±1

Because of the higher SSA in S1 and S2, the calcium content found on their surface is lower than that found in the sorbent without LGS.

Figure 4 corresponds to an image of calcium in S9 obtained with the X-Ray detector over the SEM image. It can be observed the uniform distribution on the surface of the clay.

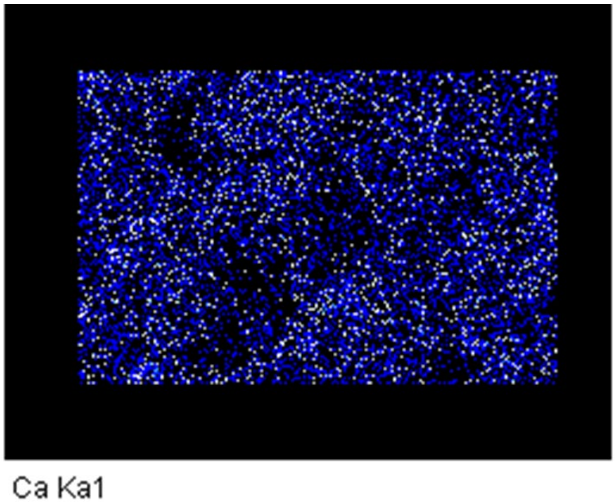


Figure 4. Calcium distribution image of S9 (sorbent without LGS) obtained with the X-Ray detector.

3.2. Desulfurization Activity. Figure 5 shows the breakthrough curve of SO_2 for S1. Similar breakthrough curves were found for the rest of the sorbents. The areas over the curves were used to calculate the values of calcium utilization, by using equation 1.

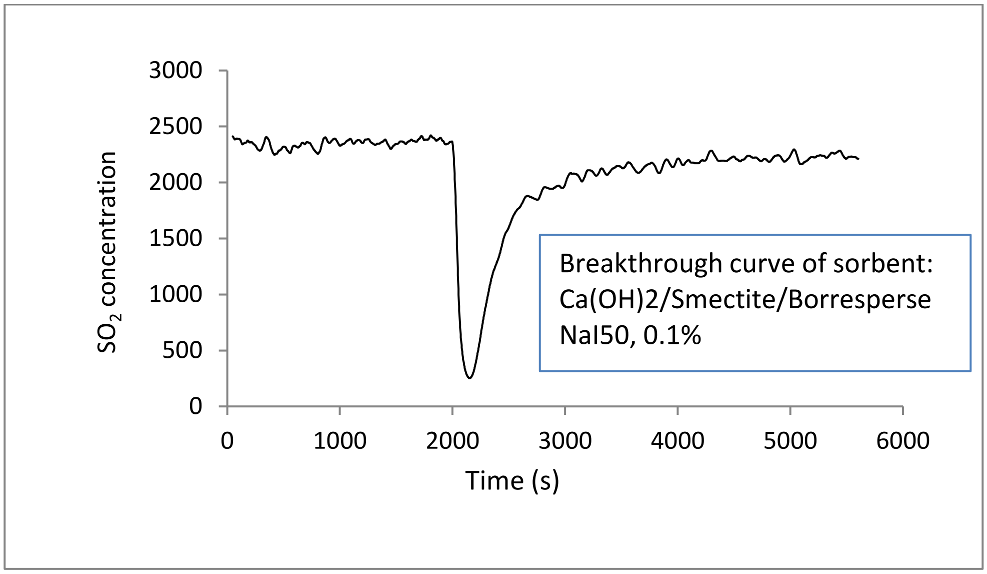


Figure 5. Breakthrough curve of the S1 solid.

Figure 6 shows the duplicated calcium utilization results obtained with all the solids. Values obtained show a good reproducibility, with maximum calculated standard deviations of 0.9. Compared to 12.8% of calcium utilization of commercial $Ca(OH)_2$, the value of 24.5% obtained with the S9, supposes an enormous increase that is attributed to the uniform $Ca(OH)_2$ dispersion on the smectite support.

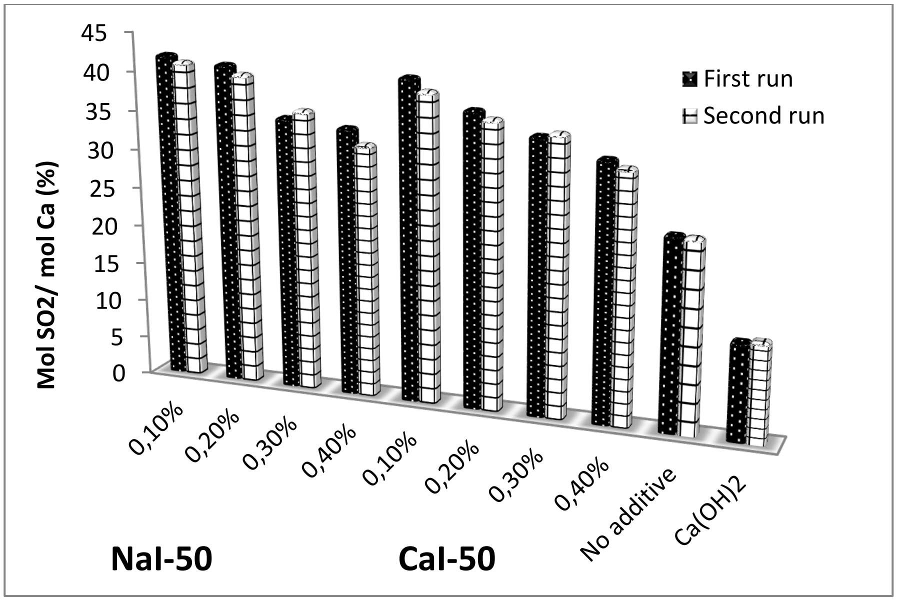


Figure 6. Calcium utilization of the sorbents, of the solid prepared without additive, S9 (blank) and of $Ca(OH)_2$.

The sorbents prepared with lignosulfonates present, respect to the S9 (sample without additive), a relevant increase in the Ca utilization with values from 31 to 42% depending on the type and amount of LGS. The highest Ca utilization (42%) was obtained with the S1, with an increase of 71.4 % respect to the solid prepared without additive (S9), being a 228% the increase respect to the commercial calcium hydroxide. No relevant differences were found between sorbents prepared with the same amount of both additives. A continuous reduction in the SO_2 capture as the amount of LGS increases was found, showing that the optimal LGS amounts are the lowest

(0.1 or 0.2%). A bibliographic review[15-18], shows discrepant optimal amounts of lignosulfonates, from 0.5-1% to 10% in weight respect to the final dry product, to be used in the synthesis of good desulfurant sorbents. When Borresperse CaI-50 or Borresperse NaI-50 lignosulfonates were used to prepare sorbents by hydration of fly ash and calcium hydroxide at 90º C [20], the optimal amounts were 0.1 or 0.2% and the same values have been found in the present work when these LGS has been used to prepare sorbents at different experimental conditions and with different raw materials. These results indicate that the optimal amount of lignosulfonates to increase the surface area and the SO_2 capture depends on the raw materials and on the experimental conditions as temperature, amount of water, way of LGS addition, drying temperature etc., used to prepare the sorbents.

Considering the best desulfurization result (42%, 42 mole of $Ca(OH)_2$ reacted per 100 mole of initial commercial $Ca(OH)_2$), and the composition of the sorbent, 1g $Ca(OH)_2$/10g Smectite, the composition of the spent sorbent for this experiment is about 5.0% $Ca(OH)_2$, 6.3% $CaSO_3.1/2\ H_2O$ and 88,7% smectite; for lower desulfurization values of remaining calcium hydroxide content will be a little bit higher and the desulfurization product $CaSO_3.1/2\ H_2O$ and smectite lower, without relevant differences among them. The composition of this waste allows using it as beneficial soil amendment at the recommended or usual soil pH[25]. Taking into account the industrial coal combustion, the waste will also contain fly ash in high amounts that must be considered. Different works[26,27] have studied the valorisation of the residue of thermal power plants, being one of these the use as a potential nutrient supplement for degraded soils. The products of the desulfurization process described in this work do not change the valorisation options summarized in these works.

Figure 7 shows the relationship between the SSA and the calcium utilization for the sorbents prepared with LGS, S1 to S8, and for calcium hydroxide or S9 prepared without LGS.

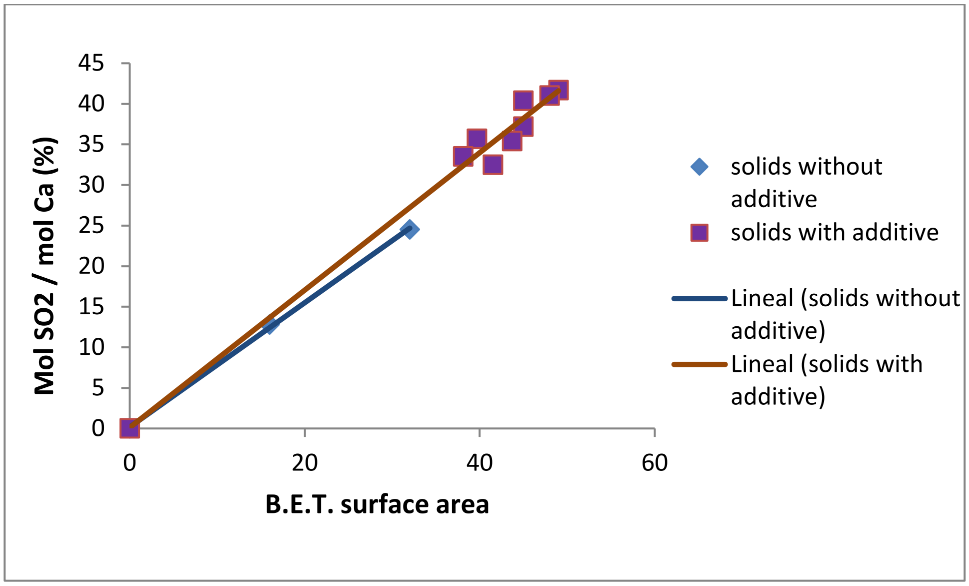


Figure 7. Relationship between the calcium utilization and the BET SSA for the solids prepared with LGS, S1-S8 and for S9 and $Ca(OH)_2$.

This figure shows a linear relationship for the S1 to S8 sorbents and another line for the S9 and $Ca(OH)_2$. As can be expected in a gas-solid reaction, the SO_2 capture increases as the SSA of the sorbent does. But this graphic shows that the slope of the line of the sorbents with LGS is slightly higher than the other one, suggesting that for solids with the same SSA, with and without LGS, the former are more reactive. This fact could be attributed to the hygroscopic properties of LGS that becomes apparent in the desulfurization reaction, retaining the humidity of the flue gas and increasing slightly the SO_2 capture.

4. CONCLUSION

In this study, it has been found that the use of the lignosulfonates Borresperse NaI-50 or Borresperse CaI-50 at concentrations of 0.1 to 0.4 weight %, in the preparation of desulfurant sorbents, by wet mixture of calcium hydroxide and magnesic smectite at room temperature, increases the porosity and the SSA and improves the SO_2 retention compared to the sorbent prepared without LGS or to commercial calcium hydroxide. The optimal results have been obtained with amounts of 0.1-0.2 weight % respect to the total solid weight, with both LGS.

The increase in the porosity and in the SSA values found when LGS are used is considered the main factor to explain the higher SO_2 retention values, but it should also be considered the hygroscopic properties of these additives that retaining more efficiently the humidity of the flue gas can also contribute to increase the SO_2 capture.

According to the composition of the spent sorbents, these would be classified as non-hazardous wastes and could be used as soil amendment.

The use of LGS in the preparation of calcium based sorbents is a good and easy way to improve their desulfurant behaviour and another promising option to valorise this lignocellulosic waste.

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REFERENCES

(1) The Spanish Electricity System, preliminary report (accessed May 4, 2016) http://www.ree.es/sites/default/files/downloadable/preliminary_report_2014.pdf

(2) Directive 2010/75/EU of the European Parliament and of the Council on Industrial Emissions (Integrated Pollution Prevention and Control). *Official Journal of the European Union Directives*.

(3) Renedo, M.J.; Fernandez, J. Preparation, Characterization, and Calcium Utilization of Fly Ash/$Ca(OH)_2$ Sorbents for Dry Desulfurization at Low Temperature. *Ind. Eng. Chem. Res.* **2002**, *41*, 2412-2417.

(4) Dahlan, I.; Mohamed, A.R.; Karamuddin, A.H.; Lee, K.T. Dry SO_2 Removal Process Using Calcium/Siliceous-Based Sorbents: Deactivation Kinetics Based on Breakthrough Curves. *Chem. Eng. Technol.* **2007**, *30*, 663-666.

(5) Renedo, M.J.; González, F.; Pesquera, C.; Fernández, J. Study of Sorbents Prepared from Clays and CaO or $Ca(OH)_2$ for SO_2 Removal at Low Temperature. *Ind. Eng. Chem. Res.* **2006**, *45*, 3752-3757.

(6) del Valle-Zermeño, R.; de Montiano-Redondo, J.; Formosa, J.; Chimenos, J.M.; Renedo, M.J.; Fernández, J. Dry desulfurization using MgO by-products: a sustainable alternative. *Energy Fuels* **2015**, *29*, 3845-3854.

(7) Fernández, J.; Rico, J.L.; García, H.; Renedo, M.J. Development of sorbents for SO_2 capture prepared by hydration of fly ash and hydrated lime in sea water. *Ind. Eng. Chem. Res.* **2006**, *45*, 856-862.

(8) Glasser, W. G.; Northey, R.A., Schultz. *ACS Symposium Series* 742, T. P. Editors, 2000. Lignine: Historical, Biological and Materials Perspectives.

(9) Rixon, M. R. Aditivos para hormigones. Composición, Propiedades y Empleo, Editores Técnicos Asociados, Barcelona, 1984.

(10) Rodsrud, G.; Lersch, M.; Sjode, A. History and future of world's most advanced biorefinery in operation. *Biomass Bioenerg.* **2012**, *46*, 46-59.

(11) Zhong, X.; Qian, Y.; Huang, J.; Yang, D.; Deng, Y.; Qiu, X. Fabrication of Lignosulfonates Vesicular Reverse Micelles to Inmobilize Horseradish Peroxidase. *Ind. Eng. Chem. Res.* **2016**, *55*, 2731–2737.

(12) Ding, P.; Garret, M.; Loe, O.; Nienow, A.W.; Pacek, A.W. Generation of Hydrogen Gas during the Catalytic Oxidation of Sodium Lignosulfonate to Vanillin: Initial Results. *Ind. Eng. Chem. Res.* **2012**, *51*, 184-188.

(13) Rodrigues Pinto, P.C.; Borges da Silva, A.; Rodrigues, A.E. Insights into Oxidative Conversion of Lignin to High-Added-Value Phenolic Aldehydes. *Ind. Eng. Chem. Res.* **2011**, *50*, 741-748.

(14) Alonso Rubio, M.V. Ph.D. Thesis, Universidad Complutense de Madrid, 2002.

(15) Kirchgessner, D.A.; Jozewicz, W. Enhancement of reactivity in surfactant-modified sorbents for sulfur dioxide control. *Ind. Eng. Chem. Res.* **1989**, *28*, 413-418.

(16) Ghosh-Dastidar, A; Mahuli, S. K.; Agnihotri, R.; Fan, L.S. Investigation of High-Reactivity Calcium Carbonate Sorbent for Enhanced SO_2 Capture. *Ind. Eng. Chem. Res.* **1996**, *35*, 598-606.

(17) Adánez, J.; Fierro, V.; García-Labiano, F.; Palacios, J.M. Study of modified calcium hydroxides for enhancing SO_2 removal during sorbent injection in pulverized coal boilers. *Fuel* **1997**, *76*, 257-265.

(18) Tseng, H-H.; Wey, M-Y.; Lu, C-Y. The study of modified Calcium Hydroxides with Surfactants for acid Gas removal During Incineration. *Environ. Technol.* **2002**, *23*, 109-119.

(19) Zhao, R.; Liu, H.; Ye, S.; Xie, Y.; Chen, Y. Ca-Based Sorbents Modified with Humic Acid for Flue Gas Desulfurization. *Ind. Eng. Chem. Res.* **2006**, *45*, 7120-7125.

(20) Renedo, M.J.; Fernández, J. Influence of Different Lignosulphonates on the Properties of Desulfurant Sorbents Prepared by Hydration of Ca $(OH)_2$ and Fly Ash. *Ind. Eng. Chem. Res.* **2008**, *47*, 1331-1335.

(21) Pinnavaia, T.J.; Amarasekera, J. Hydrated lime clay composites for the removal of SO_x from flue gas streams. US Patent 5 298 473, 1994.

(22) Goldberg, D.; Roystob-Browne, A. Composition, production et utilisation de particules de sorbant pour la desulfuration de gaz d'echappement. CA Patent 2695275 A1, 2009.

(23) Renedo, M.J.; Fernández, J. Procedimiento para la obtención de un sorbente captador de SO_2. ES Patente 2 336 636 B1, 2010.

(24) Renedo, M.J.; Fernández, J. Use of TG-DSC-MS and gas analyzer data to investigate the reaction of CO_2 and SO_2 with $Ca(OH)_2$ at low temperature. *Chem. Eng. Trans.* **2013**, *35*, 739-744.

(25) Ritchey, K.D., Kinraide, T.B., Wendell, R.R. Interactions of calcium sulfite with soils and plants. *Plant Soil* **1995**, *173*, 329-335.

(26) Pandey, V.C., Singh, N. Impact of fly ash incorporation in soil systems. *Agriculture, Ecosystems and Environment* **2010**, 136, 16–27

(27) Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S., Xi, Y.Q. A comprehensive review on the applications of coal fly ash. *Earth-Science Reviews* **2015**, 141, 105–121.