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Use of Ash from Sewage Sludge in the Preparation of Desulfurant Sorbents*

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Abstract

This work aims to develop new uses for sewage sludge, which is a byproduct of municipal wastewater treatment plants, by examining the calcination of this waste, the characterization of ashes is obtained, and its use to prepare desulfurant sorbents. Samples of sewage sludge were obtained from a local municipal wastewater treatment plant. This plant applies a pre-treatment followed by a biological treatment, where anaerobic digestion and centrifugation reduces the sludge. Three samples were characterized (in humidity, volatile and fixed solids content), dried, and ignited at two temperatures, 550 and 750°C. The composition of the ash obtained at both ignition temperatures was studied by x-ray fluorescent spectroscopy and the BET specific surface area of the two ashes and of the prepared sorbents was measured. Ash composition was similar for the two temperatures tested, where the components were Si, Ca, Al, Fe, P, S, Mg, K, Cl, Zn and Ti. BET specific surface area values indicate that the lower temperature of calcination produces ash with the highest SSA values (18 m²/g against near 10 m²/g). Preparation of desulfurant sorbents was carried out by mixing the ash with CaO or Ca(OH)₂ at room temperature and different experimental conditions. The BET SSA of the prepared desulfurant sorbents showed higher values for the sorbents prepared with the ashes obtained at the lowest temperature. The behaviour of the ash and the prepared sorbents was tested in a fixed bed reactor at 58°C with a flue gas containing 5000 ppm of SO₂ with a relative humidity of 55%. Results in the desulfurization process show that the calcium from the sludge seems more efficient than the calcium added as CaO or Ca(OH)₂ to prepare the sorbents.

KEYWORDS: sewage sludge, calcination, desulfurization sorbent

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1. INTRODUCTION

Sewage sludge is the waste left behind after cleaning wastewater. This sludge consists of a complex heterogeneous mixture of organic and inorganic compounds ((Metcalf, E., 2002). In recent years, the number of wastewater treatment plants and consequently the production of sewage sludge has increased, being the problem of sewage sludge disposal one of the most complex environmental problems, which must be resolved in accord with the sustainable development principle.

In the developed countries, most of the sewage sludge waste is disposed off in landfills, oceans, or via incineration, none of which are exempt from drawbacks (Werther, J. and Ojada, T, 1999). In Spain, the common way of management and valorisation of sewage sludge has been the agricultural use. However, due to the legislation in the European Community not all the sewage sludge can be used as fertiliser and a relevant amount of this sludge is incinerated to reduce the volume of waste. According to the current treatments applied to the sludge, the II Wastewater Sewage Sludge National Plan in Spain (EDAR II-PNLD 2007-2015) provides, as one of its objectives, to increase the efficiency in the treatments carried out in the wastewater plants to optimize the recovery of sludge. The production of sewage sludge in Spain was near 1.2 millions of dry tons in 2005 being the energetic valorisation, the reuse and the agricultural use some valorisation options expressed in this National Plan.

There is a growing body of literature (Murray et al., 2008, Chow, J-D et al, 2006 and Elías Castell, X. 2000) that looks at the costs and benefits of using sludge and sludge treatment byproducts as raw materials in different production processes: as cement additive, road building material or ceramic material. Recently, the option of recycling the sewage sludge in the form of adsorbents or reactive adsorbents has also been considered (Kante, K. 2008) .

The composition of the sewage sludge of a wastewater treatment plant in Santander (Spain) has been previously studied (Fernández, J. et al, 2008 and Fernández, J. et al, 2008). This wastewater treatment plant was designed for a regular flow rate of 8100 m³ / h with average suspended solids content of 230 mg / l and average DBO₅ of 200 mg / l. The wastewater treatment consists in a pre-treatment followed by an aerobic biological treatment of high organic loading rate and settlement tanks. After that, clean water is sent to the sea and the sludge goes to a thickener followed by an anaerobic treatment and a final dehydration by centrifugation. The sludge is stored and transported to a municipal landfill. A sludge drying plant, as a first step to minimize this waste, has been constructed and is beginning its operation.

According to these previous results and with the objective of developing new uses of sewage sludge, the purpose of the present work was, after a new

sludge characterization, the calcination of this waste at two temperatures (550 and 750° C), the characterization of the ash obtained and its use to prepare desulfurant sorbents.

2. EXPERIMENTAL PROCEDURE

2.1 SLUDGE TREATMENT AND ASHES CHARACTERIZATION.

Three samples of the final sewage sludge were taken off from the local municipal wastewater treatment plant at three different weeks. These samples were analyzed in triplicate.

The sewage sludge characterization carried out included the determination of the following parameters: humidity, total solids content (TS), fixed solids (FS), volatile solids (VS) and pH. All these parameters were measured by following procedures outlined in the Standard Methods (APHA/AWWAWEF, 2005) pH value was obtained in a 10% aqueous solution of the wet sludge with a pH-meter MicropH 2002 Crison according to the UNE-EN 12176, 1998 procedure.

Humidity was determined drying a well-mixed sample of sewage sludge to constant weight in an oven at 105°C. The residue obtained from the humidity determination (dry sludge) was ignited to constant weight at 550°C or 750° C in a Heron HK-11 oven for two hours. The remaining solids represent the fixed total solids (FS) while the weight lost on ignition is the volatile solid (VS). The obtained ashes were milled in a mortar and sieved through a 80 µm mesh.

Characterization of the ash obtained after calcination consisted in the determination of the composition by X-Ray Fluorescent Spectroscopy with an ARL Advant-XP equipment.

The specific surface area of the ash and of the prepared sorbents was obtained by using the B.E.T. method in a Micromeritics Asap 2000 equipment.

2.2 PREPARATION OF THE SORBENTS

Six different sorbents were prepared and studied. All these sorbents were obtained by mixing CaO or Ca(OH)₂ and sludge-ash at room temperature and at a constant calcium base / ash ratio of 1/10. For sorbents prepared by wet mixture a solid /water ratio of 1/10 was used. In this sorbents CaO and ash were stirred with water for 15 minutes. After, the slurry was filtered through a 0.42 µm mesh and dried 24 hours at 110° C. Dry sorbents were prepared by mixing manually raw materials.

Table I shows the experimental conditions used to calcinate the sludge and to prepare the sorbents

Table I. Experimental conditions used in the preparation of sorbents.

Sorbent identification	1	2	3	4	5	6
Temp. of the sludge calcination	550	550	550	750	750	750
Calcium base	Ca(OH) ₂	CaO	CaO	Ca(OH) ₂	CaO	CaO
Mixing procedure	dry	dry	wet	dry	dry	wet

2.3 SULFATION TEST

Desulfurization behaviour of the obtained sorbents was quantified as (mol of SO₂ captured / mol of Ca in the sorbent) x 100. As the number of moles of SO₂ captured is the same as the number of mol of Ca reacted the former expression is the calcium utilization in the desulfurization process or calcium conversion. This calcium utilization was obtained from the reaction between the solid and SO₂. Experiments were carried out in the setup depicted schematically in Figure 1.

Approximately 1 g of the sorbent was weighed and dispersed manually in 30 g of an inert silica sand bed and the whole bed was supported on a 3.6 cm diameter fritted glass plate contained in the glass jacketed fixed-bed reactor.

The volume composition of the gas was: 5000 ppm SO₂, 12% CO₂, 2% O₂ and balance N₂ and a rate of 1000 cm³/ min. The gas stream without SO₂ passed through the humidification system where it was in contact with water in two absorber flask. After humidification, the gas mixture at a relative humidity of 55% and with SO₂, flowed through the reactor maintained at 58° C. This temperature was used to simulate industrial desulfurization process post combustion at low temperature. To retain the remaining water, the gas stream leaving the reactor was led to the “water condensation system” before passing through the continuous NGA2000 MLT1 Emerson SO₂ analyser.

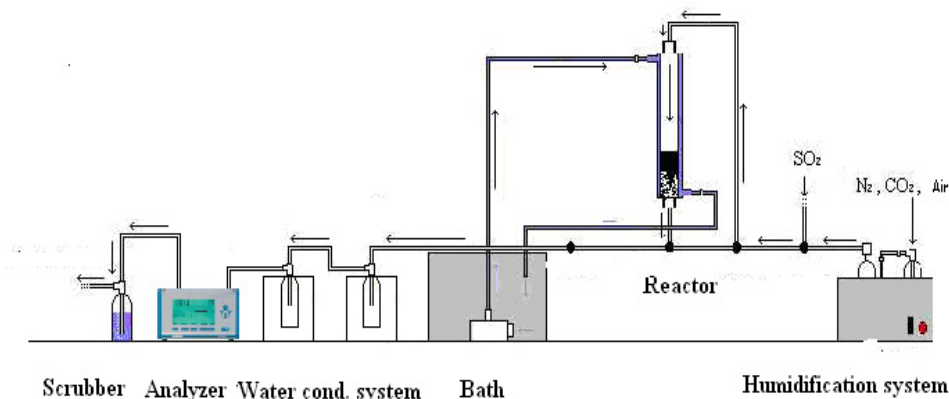


Figure 1. Experimental setup.

The concentration of SO₂ was continuously monitored with a personal computer equipped with a NGA win control software and breakthrough curves of SO₂ concentration in the gas stream leaving the reactor were plotted. After passing through the analyser, the flue gas was led to a scrubber with a Na(OH) solution to retain the remaining SO₂.

When the reaction time was over (controlled by the breakthrough curves), the reaction product was sieved to separate the reacted sorbent from the sand, and the reacted sorbent was analyzed by the thermogravimetric technique (TG) to obtain the amount of SO₂ captured. For this determination, a Perkin-Elmer TGA-unit with the following temperature furnace program was used:

Temp 1: 20° C	Time: 1.0 min	Rate: 20.0° C/min
Temp 2: 600° C	Time: 20.0 min	Rate: 20.0° C/min
Temp.3: 1300° C	Time: 100.0 min	

A personal computer with a Perkin Elmer Pyris program was used to obtain the results of the analysis. Synthetic air was used as carrier gas (30 cm³/min). The sample weight was always between 10 and 20 mg. TG curves of the reacted sorbent showed a weight loss between 850 and 1300°C, that was attributed to the

calcium sulphate decomposition in $\text{CaO}_{(s)}$ and $\text{SO}_{3(g)}$. This analysis allowed the calculation of the calcium utilization quantified as calcium conversion.

2.4 CALCIUM CONVERSION

Calcium conversion values quantified as mol SO_2 captured/ mol Ca in the sorbent was obtained by using the breakthrough curves of SO_2 and by thermogravimetric analysis of the reacted sorbents. In this last case next equation is used:

$$\frac{\frac{\text{moles of SO}_2 \text{ captured}}{\text{grams of sorbent}}}{\frac{\text{moles of calcium}}{\text{grams of sorbent}}} = \frac{\left(\frac{\% \text{ SO}_3}{100} - \frac{\% \text{ of ash}}{100} * \frac{\text{g of ash}}{\text{g of sorbent}} \right) \frac{1 \text{ mole SO}_3}{80 \text{ grams SO}_3}}{\frac{\text{moles of calcium}}{\text{grams of sorbent}}}$$

Values of % SO_3 and % of ash are obtained from the TG curves of the reacted sorbent and of the unreacted (sludge 550°C after capture SO_2 or sludge 550°C) in Figure 2, respectively considering the mass loss in the range of temperatures of 850-1300.

Figure 2 shows TG curves of the ash obtained at 550°C before and after SO_2 capture (sludge 550°C after capture SO_2 or sludge 550°C) and of the sorbents 2 and 3 prepared with this ash after capture SO_2 .

The moles of calcium/grams of sorbent, were calculated in two ways: a) considering the amount of calcium in the ash and the amount of calcium added, (Conversion T.G. % (1) in Table V), or b) considering only the calcium added as that is the calcium relevant from an economical point of view. (Conversion T.G. % (2) in Table V).

The SO_2 captured from the breakthrough curves was obtained calculating the area over this breakthrough curve.

3. RESULTS

3.1 CHARACTERIZATION OF SLUDGE, ASHES AND PREPARED SORBENTS

Table II shows the results of the characterization of the sludge ignited at 550°C and 750°C .

These results are medium values of three different sludge samples analyzed each by triplicate

Table II. Characterization of the dry sludge submitted to ignition at two temperatures

Sludge calcination temperature	Humidity % in the sludge	Volatile solids % of the total solids	Fixed solids % of the total solids	pH
550° C	71	45	55	10.24
750° C	71	47	53	10.04

These results show very similar values for the parameters studied with a slight increase in the volatile solids content as the ignition temperature increases due to the loss of some compounds in the range of temperature between 550 to 750° C.

After calcination and milling the dry sludge, the composition of the obtained ash at both ignition temperatures was obtained by XRF spectroscopy. Results are shown in Table III for the main 11 elements.

Table III: Elemental composition in weight % for the main elements found in the ash obtained by calcination of sludge at 550 and 750 ° C.

Element	Si	Ca	Al	Fe	P	S	Mg	K	Cl	Zn	Ti
Weight % (550° C)	12.8	15.56	6.74	8.76	4.49	2.55	2.17	1.36	1.05	0.623	0.452
Weight % (750° C)	13.2	16	6.96	8.58	4.56	2.07	2.14	1.37	0.555	0.61	0.456

Results of Table III correspond to the mixture of 3 samples of ash obtained by calcination of sludge at 550 or 750 ° C.

As could be expected no relevant differences were found within the ash depending on the calcination temperature. It is remarkable the high weight percent of calcium in both ashes due, at least in part, to the addition of $\text{Ca}(\text{OH})_2$ in the anaerobic step to maintain basic values of pH.

Specific surface area values of the ash and of the sorbents were obtained as this parameter is relevant in the process of the retention of gases. Table IV shows these BET specific surface values. The sorbents are identified according to the experimental conditions used in the process of preparation. The meaning of the identification number is shown in Table I.

Table IV. BET Specific surface area values for ash and for the sorbents.

	Ash 550° C	Ash 550° C	Sorbent 1 (550)	Sorbent 2 (550)	Sorbent 3 (550)	Sorbent 4 (750)	Sorbent 5 (750)	Sorbent 6 (750)
BET surface area (m²/ g)	18.3	9.9	14.4	15.5	19.0	8.7	9.1	9.5

Table IV shows that specific surface area of the sorbents is related to the surface area of the sludge-ashes used in the preparation of the sorbents. The highest value corresponds to sorbent 3 prepared by wet method.

3.2 DESULFURIZATION BEHAVIOUR

As has been explained in the experimental section, calcium conversion in the sorbent was calculated by using thermogravimetric data and from the breakthrough curves.

Figure 2 shows the TG curves of the sludge calcinated at 550 ° C before and after being used to capture SO₂, (black and green colours) as well as TG curves of sorbents 2 and 3 prepared with the sludge calcinated at 550° C after being used to capture SO₂.

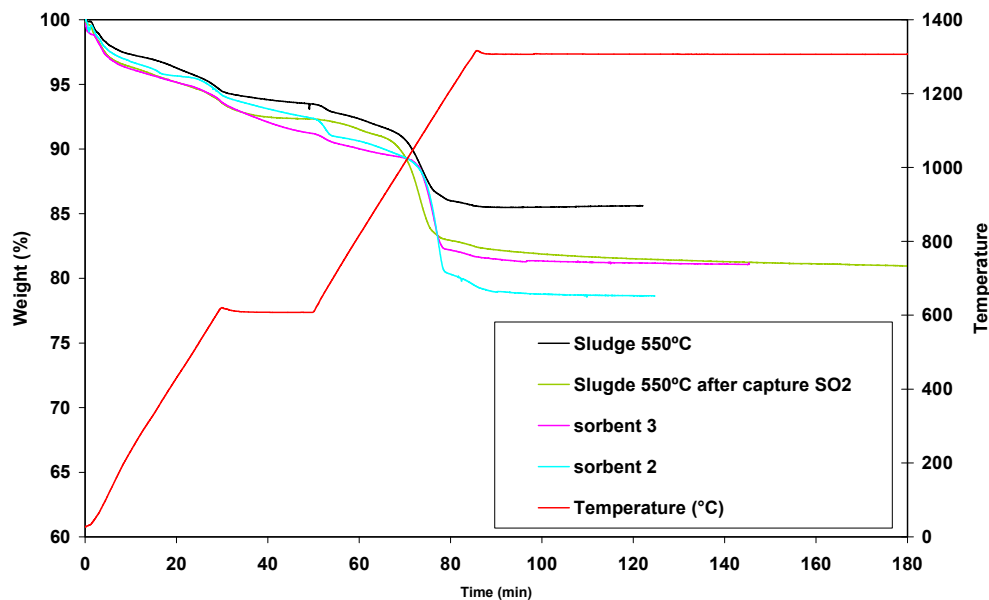


Figure 2. Thermogravimetric curves of the sludge ignited at 550° C before and after being capture SO₂ and of sorbents 2 and 3 after SO₂ capture

As Figure shows the calcinated sludge (sludge 500° C), suffer a mass loss within 61 and 180 minutes that correspond at a range of temperature within 850 and 1300°C. This mass loss is not due to the release of SO₃ formed in the calcium sulphate decomposition and must be attributed to the decomposition of components of the ash. Because of that in the expression to calculate the calcium conversion, the mass loss of the ash, as % of ash, is subtracted from that due to the decomposition of SO₃ as has been explained in the experimental section.

Table V shows the desulfurization results obtained with the ashes used to capture SO₂ and with the sorbents, with both experimental techniques, TG and SO₂ breakthrough curves.

Table V. Calcium conversion values obtained by Thermogravimetry and from breakthrough curves (SO₂ Curve), for the ash obtained at 550° C or 750° C and for the sorbents. (1) Results obtained considering all the calcium of the sorbents. (2) Results obtained considering only the calcium added to prepare the sorbent.

Sorbent identification	Conversion (T.G.) % (1)	Conversion (T.G.) % (2)	Conversion (SO ₂ Curve)% (1)
Ash obtained at 550° C	15,8	15,8	13,3
Ash, 550° C+ Ca(OH) ₂ (1)	12,5	52,1	13,9
Ash, 550° C+ CaO Dry (2)	14,7	50,4	16,6
Ash, 550° C+ CaO Wet (3)	7,2	24,6	10,5
Ash obtained at 750° C	5,8	5,8	5
Ash, 750° C + Ca(OH) ₂ (4)	7	29,6	8,5
Ash, 750° C+ CaO Dry (5)	5,3	18,6	5,9
Ash 750° C+ CaO wet (6)	3,1	10,8	4,7

As Table shows calcium conversion results obtained from the breakthrough curves are, in general, higher than that obtained by thermogravimetry when both values are calculated considering all the calcium present in the sorbent.

Conversion value obtained with commercial Ca(OH)₂ tested at the same experimental conditions is about 15%. This result is similar to that obtained with the ash prepared by calcination at 550° C, with no calcium added, and higher than those obtained with the sorbents, when the conversion values are calculated considering all the calcium present in the sorbent (Conversion T.G.% (1)). If, in the calculation of the calcium conversion, is only considered the calcium added, Table V shows higher values (Conversion T.G.% (2)) for all the sorbents except for the last one, comparing to the conversion found with commercial Ca(OH)₂.

Considering desulfurization results obtained with the ash (sludge ignited) and with the sorbents prepared with the ash, (Conversion T.G.% (1)) it must be concluded that is more efficient the calcium coming from the ash than the added calcium, as conversion values of these sorbents are slightly lower than those obtained with the ash alone.

Comparing the ash obtained at 550 and the sorbents prepared from this ash, to the ash obtained at 750° C and the sorbents prepared with that ash, Table V shows that is more efficient the ash obtained at 550° C and the sorbents prepared with this ash, than the ash obtained at higher temperature and the sorbents prepared with this ash. An explanation of this behaviour is the higher specific surface area values, see Table IV, of the ash obtained at 550°C and of the sorbents

prepared with this ash, comparing to the surface areas of ash obtained at 750° C and of the sorbents prepared by using this ash.

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