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Addition of $CaCO_3$ in the Incineration of a Wastewater Sludge at 900º C. Preparation of Desulfurant Sorbents With the Incinerated Sludge

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With the aim of developing new uses of sewage sludge, a byproduct of municipal wastewater treatment plants, in the present work the calcination at 900º C of this waste with or without $CaCO_3$ added was performed; the sludge was obtained from a local municipal wastewater treatment plant. The purpose was to study the ability of the $CaCO_3$ to capture SO_2 during the incineration. The resulting ashes were reactivated at different experimental conditions to obtain desulfurant sorbents to be used in a further desulfurization process at low temperature.
The humidity, total solids and fixed and volatile solids were determined in the sludge with and without $CaCO_3$ added. The elementary analysis of the dry sludge and of the calcinated was obtained. Results show that the C percentage highly decreases in the incineration due to the release of the volatile carbon compounds. The sulphur percentage increases principally due to the release of the volatile matter. The resulting ashes with or without $CaCO_3$ added were studied by Thermogravimetry. T.G. curves show that not all the $CaCO_3$ was calcinated mainly when the amount of $CaCO_3$ added was high. The specific surface area of the dry sludge, of the ashes and of the sorbents prepared by reactivation of the ashes was also determined.

1. Introduction

Sewage sludge is a biomass by product of municipal wastewater treatment plants. It has to be disposed in significant amounts in all developed countries and so far it has been mainly used as a landfill material, road building material, fertilizer or cement additive. Nevertheless most of this sludge is still incinerated to reduce the volume of waste.
In Spain, the II Wastewater Sewage Sludge National Plan (EDAR II-PNLD 2007-2015) shows as an objective the minimization of the deposition of the sewage sludge. According to this objective, the agricultural use of the best quality of sewage sludge and other valorisation forms (energetic, co incineration) must be achieved.
The wastewater treatment plant in Santander (Spain) operates according to a pre-treatment followed by a biological treatment, being the sludge reduced by an anaerobic digestion and centrifugation. With the objective of developing new uses of sewage sludge, in a previous work, Fernández et al., (2009), submitted the dry sludge to

calcination at two temperatures (550 and 750º C); the resulting ashes mixed with $Ca(OH)_2$ were used as desulfurant sorbent in a desulfuration process at low temperature. The purpose of the present work was to incinerate the sludge at 900º C to simulate an industrial incineration process usually performed at least at 850º C to convert organic matter into gases. $CaCO_3$ was added to study their ability to capture the SO_2 produced in the incineration. The sludge submitted to incineration as well as the resulting ashes with or without $CaCO_3$ added were characterised.
These resulting ashes were used to prepare desulfurant sorbents to be used in a desulfurization process at low temperature.

2. Experimental Section

2.1 Sludge and ash characterization

Three samples of the 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). TS, FS and VS values were obtained after the incineration of the sludge with or without $CaCO_3$ added. All these parameters were measured by following procedures outlined in the Standard Methods , APHA/AWWAWEF, (2005)
Humidity was determined drying a well-mixed sample of sewage sludge to constant weight in an oven at 105ºC. After the determination of humidity and T.S all the samples of sludge were mixed to have a unique sample of sludge in further experiments.
The dry sludge with $CaCO_3$ added at different sludge/$CaCO_3$ ratios, 10/0, 10/1, and 10/10 was ignited in a furnace at the usual sludge incineration temperature of 900º C to constant weight (three hours approximately). The amount of solid after ignition represents 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 63 μm mesh.
The samples obtained in the furnace, solids 1, 2 and 3 with a initial sludge/$CaCO_3$ ratios of 10/0, 10/1, and 10/10 respectively were characterized by thermogravimetry using a Perkin-Elmer TGA-unit with a temperature furnace program between room temperature to 1250 °C, and a Pyris program (software from Perkin Elmer) were used, with synthetic air as carrier gas (30 cm^3/min). From the thermal analysis data, the amount of SO_2 retained during the ignition was also known. Results of the SO_2 capture are reported in other communication at this Congress ((Renedo M.J. and Fernández, J (2010).
The dry sludge and the sludge after calcination at 900 ºC were submitted to an elementary analysis to know the C and S content. Values of C and S for the sludge calcinated at 550 or 750 ºC are also reported to compare results obtained at different incineration temperature. The specific surface area of the dry sludge and of the solids 1, 2 and 3, was obtained by using the B.E.T. method in a Micromeritics Asap 2000 equipment.

2.2 Preparation and characterization of sorbents for desulfurization at low temperature

Sorbents to be used in a desulfurization process at low temperature were prepared by reactivation of solids 1, 2 and 3 obtained in the incineration step.

Different ways to reactivate the samples of ashes were tried. The aim was to obtain a sorbent with a high capacity to retain SO_2 at low temperature.

Table 1 shows the reactivation conditions essayed. Only the sorbent 5 was prepared by mixing in water, new calcium base, CaO, and the ashes. The rest of the sorbents were obtained by hydration of the ashes containing the remaining $CaCO_3$ at different times and temperatures.

Table 1: Reactivation conditions of the solids 1, 2 and 3 obtained in the furnace

Solids composition	*Number of reactivated sorbent*	*Reactivation conditions*
Ashes from (10g dry sludge + 1g $CaCO_3$) +10 mL H_2O	1	90 ºC, 7 hours
Ashes from (10g dry sludge + 10g $CaCO_3$) +10 mL H_2O	2	90 ºC, 7 hours
Ashes from (10g dry sludge + 1g $CaCO_3$)+ 10 mL H_2O	3	Room temperature 15 minutes
Ashes from (10g dry sludge + 10g $CaCO_3$)+10 mL H_2O	4	Room temperature 15 minutes
10g ashes +1g CaO +7ml H_2O	5	90 ºC , 7 hours

As the capture of SO_2 from a flue gas with a solid is a gas-solid reaction, it could be thought that the sorbent with the highest specific surface area should be the best in the desulfurization reaction. Because of that, after the reactivation process, the specific surface area was determined for all the prepared sorbents.

3. Results

3.1 Characterization of sludge and of the ashes

Table 2 shows the humidity and total solids content (TS) of the sludge collected in different days. Values in Table 2 show a great similarity in the humidity and solids content of the different samples of the sludge.

Table 2: Values of humidity and total solids obtained from 3 samples of sludge analysed by triplicate.

Sample	*Humidity*	*Total solids content*	*Mean value of humidity*	*Mean value of total solid*
Sludge 22/10/2008	70.24 %	29.76 %		
Sludge 30/10/2008	71.29 %	28.71 %	70.52 %	29.15 %
Sludge 11/11/2008	70.02 %	28.98 %		

The dry sludge obtained by mixing all the sludge samples was incinerated at 900º C and the resulting solid was named solid 1. Mixtures of dry sludge and CaCO3 at a 10/1 and 10/10 sludge/$CaCO_3$ ratio were also incinerated at the same conditions being solid 2 and solid 3 the resulting ashes. Table 3 shows the fixed solids (FS) and volatile solids (VS) obtained after incineration of the three solids.

Table 3: Fixed and volatile solids obtained after the incineration of the sludge

SAMPLE	*Volatile solids*	*Fixed solids*
Dry sludge	46.8 %	53,2 %
10 Dry sludge + 1 $CaCO_3$	47.5 %	52.5 %
10 Dry sludge+ 10 $CaCO_3$	42.6 %	57.4 %

Results of Table 3 show a higher percentage of fixed solids in the solid prepared with the highest amount of $CaCO_3$ as it could be expected.
Results of the elementary analysis of the dry sludge and of the sludge incinerated at 900 ºC are shown Table 4. Results for the sludge calcinated at 550 and 750 ºC are also included in the Table to know the influence of the temperature on the amount of C and S in the resulting ashes.

Table 4: Elementary analysis of the dry sludge and of the sludge calcinated at 550, 750 and 900 ºC.

SAMPLE	*%C*	*%S*
Dry sludge	18.18	1.53
Sludge calcinated at 900 ºC	0.040	1.88
Sludge calcinated at 750 ºC	3.14	1.84
Sludge calcinated at 550 ºC	3.97	1.77

Results of Table 4 show that as the temperature increases the percentage of C in the sample decreases due to the release of the volatile organic compounds containing carbon. At 900 ºC even the carbon as $CaCO_3$ is calcinated, as least in part, as has been proved by thermogravimetry. The sulphur percentage increases as temperature does due principally to the amount of volatile organic compounds released.
Figure 1 shows the thermogravimetric curves of the solid 1, only sludge calcinated at 900 ºC, solid 2, 10 sludge /1 $CaCO_3$, and solid 3, 10 sludge /10 $CaCO_3$.

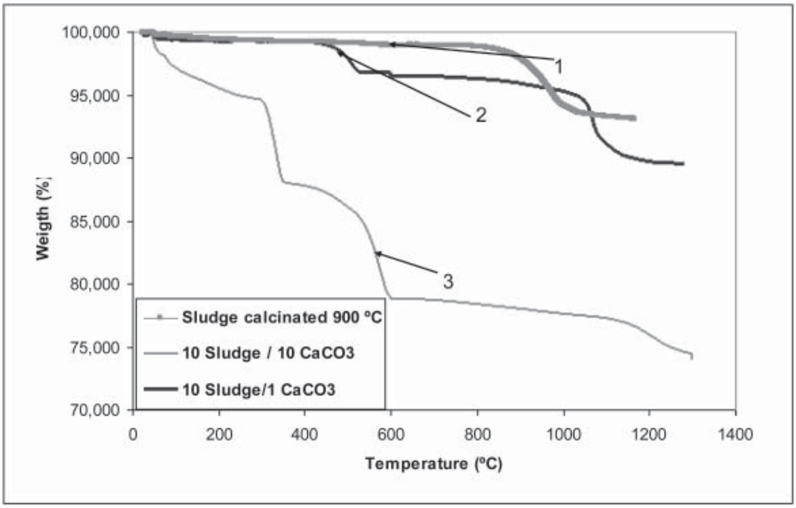

Figure 1: Thermogravimetric curves of the ashes coming from the solid 1, only sludge, solid 2, 10 sludge/1$CaCO_3$, and solid 3 , 10 sludge/10 $CaCO_3$.

The mass loss noted in the figure is due to the $CaCO_3$ decomposition in CaO and CO_2 gas. From these mass loss, the amount of $CaCO_3$ remaining in the ashes, and no calcinated during the incineration, was calculated. For solid 2, 4.47 % of the limestone was still present in the ashes, being 31 % the amount remaining when the sludge /$CaCO_3$ ratio was 10/10 in solid 3. These results show that the calcination of the limestone is not total during the incineration probably due to difficulties in the heat transfer and in the release, by diffusion, of the CO_2 formed in the calcination.
Table 5 shows the specific surface area of the three solids and of the dry sludge.

Table 5: Specific surface area of the dry sludge and of the solids 1, 2 and 3.

Solids	*Specific surface area* m^2/g.
Dry sludge	10.8
Ashes of dry sludge (solid 1)	3.8
Ashes of 10 Sludge/1 $CaCO_3$ (solid 2)	5.9
Ashes of 10 Sludge/10 $CaCO_3$ (solid 3)	3.9

A relevant reduction in the specific surface area was found when the sludge looses the volatile material in the furnace. It could be thought that as the calcination of $CaCO_3$ takes place, the mass loss, difference between the mass of $CaCO_3$ and of the CaO, should generate holes in the solid and an increase in the surface area value; but, the influence of the CO_2 production in the surface area generation is not appreciated.

3.2 Characterization of the desulfurant sorbents prepared with solids 1, 2 and 3.

Table 6 shows the values of the specific surface area of the sorbents prepared by hydration of the solids 1, 2 and 3 at the different reactivation conditions performed.

Table 6: Specific surface area of the sorbents prepared from the ashes at different experimental conditions.

Number of reactivated sorbent	*Reactivation conditions*	*SSA (m^2/g)*
1	90 ºC, 7 hours	9.1
2	90 ºC, 7 hours	10.8
3	Room temperature 15 minutes	5.9
4	Room temperature 15 minutes	4
5	90 ºC , 7 hours	18.9

As Table 6 shows, the sorbent prepared by adding new CaO and hydrated at 90 ºC, 7 hours, sorbent number 5 in the Table, corresponding to (10g Ashes +1g CaO+7 ml H_2O) in the Table 1**, s**hows the highest surface value. Apart from this sorbent prepared with new CaO added to the ashes in a no usual reactivation process, for the rest of the sorbents, a slight increase in the specific surface area values was found when the sorbent was prepared at high temperature and time.

4. Conclusions

Results obtained in the thermogravimetric study of the solid 1, obtained by calcination of 10 sludge/1 $CaCO_3$ and solids 2, obtained by calcination of 10sludge/10 $CaCO_3$ allow to conclude that not all the $CaCO_3$ added has been decomposed in CaO and CO_2, mainly when the amount of $CaCO_3$ is high as in solid 2. Respect to the specific surface area of the reactivate sorbents results show that when new CaO is added in the reactivation process, the specific surface area value is the highest.

Acknowledgment

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