Desulfurization Behaviour of $CaCO_3$ added During the Calcination of Wastewater Sludge at 900º C: Reuse of the Ash after Reactivation

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In the present work dry sewage sludge from a local municipal wastewater plant, has been incinerated at 900 º C with $CaCO_3$ added at two sludge/$CaCO_3$ ratios: 10 sludge /1 $CaCO_3$ or 10 sludge /10 $CaCO_3$ in weight. The ability of this salt to capture the SO_2 produced during the incineration is studied. The SO_2 captured is quantified as mole SO_2 / mole of Ca. Results shows that the amount of SO_2 captured /mole of $CaCO_3$, is much higher at the 10 sludge /1 $CaCO_3$ ratio. With the resulting ashes, reactivated at different ways, desulfurant sorbents were prepared and essayed in a desulfurization process at low temperature. Results of the process at low temperature showed that the highest value of SO_2 captured was found with the sorbent coming from the ashes obtained from the mixture 10 sludge /1 $CaCO_3$ and reactivated by hydration at room temperature.

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 2002). In recent years, the number of wastewater treatment plants and consequently the production of sewage sludge has increased, being the sewage sludge disposal one of the most complex environmental problems.

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 as Werther and Ojada (1999) have reported. In Spain, 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. The II Wastewater Sewage Sludge National Plan in Spain (EDAR II-PNLD 2007-2015) regulates the sewage sludge uses and establishes alternatives to the common uses of the sludge.

There is a growing body of literature (Murray et al., 2008; Chow et al., 2006; Castells 2000), that looks at the costs and benefits of using sludge and sludge treatment by-products as raw materials in different production processes. Recently, the option of recycling the sewage sludge in the form of adsorbents or reactive adsorbents has also been considered Kante et al. (2008). This valorisation option is the goal of the present work. The composition of the ash obtained by calcination at 550 ºC of the sewage

sludge of a local wastewater treatment plant has been previously studied by Fernández et al. (2008).

In the present work, dry sewage sludge of this plant with $CaCO_3$ added, has been used to study the properties of SO_2 retention. The effect of adding $CaCO_3$ during the combustion of the sludge at 900º C, in the capture of the SO_2 released in the process is studied. The aim was to simulate a desulfurization process during the combustion, by reaction of the CaO formed in the $CaCO_3$ calcination, and the SO_2.

 As not all the calcium base was used to capture SO_2 during the combustion, the solid obtained (ashes from sludge and calcium compound) was reactivated and tested as desulfurant at low temperature (58º C).

Two different process of SO_2 capture are then presented in this work: 1) Desulfurization during the sludge combustion at 900º C produced by the CaO formed by calcination of the $CaCO_3$ added. 2) Desulfurization post combustion with the reactivated ash coming from the combustion process.

2. Experimental procedure

2.1 Desulfurization during the sludge combustion

 The dry sludge with $CaCO_3$ at different sludge/$CaCO_3$ weight ratios [10/0, 10/1, and 10/10] was ignited in a high temperature oven at 900º C for two hours. During the ignition, the SO_2 released from the sulphur products present in the sludge, reacts with the CaO obtained from the $CaCO_3$ and also with a possible amorphous CaO of the sludge formed by dehydration of the $Ca(OH)_2$ added in the treatment plant.

When the ignition time was over, the solid or *sorbent* (ash + remaining $CaCO_3$ + the product of the desulfurization reaction), was cooled and the amount of SO_2 captured was quantified by thermogravimetry.

Desulfurization behaviour was quantified as (mol of SO_2 captured / mol of Ca in the sorbent) x 100. As the number of moles of SO_2 captured is the same than the number of mol of Ca reacted, the expression is the calcium utilization or calcium conversion in the desulfurization process.

To calculate the calcium conversion by thermogravimetry, a Perkin-Elmer TGA-unit with a temperature furnace program between 50 and 1300^oC was used. A personal computer with a Perkin Elmer Pyris program was use to obtain the results of the analysis. Synthetic air was used as carrier gas (30 cm^3/min). TG curves of the solid (ash + remaining $CaCO_3$ + the product of the desulfurization reaction) showed a weight loss between 850 and 1300 ^oC, that was attributed to the calcium sulphate decomposition in $CaO_{(s)}$ and $SO_{3(g)}$. At this same range of temperatures, T.G. curves of the ashes, without $CaCO_3$ added, also showed a mass loss. Because of that, and to evaluate the SO_2 retained by the $CaCO_3$ added, this mass loss was subtracted from the loss of the solid as it is explained further.

2.2 Desulfurization post combustion

After the ignition time, the resulted ash was reactivated following different procedures and these reactivated sorbents were essayed in a post combustion desulfurization process carried out in the setup depicted schematically in Figure 1.
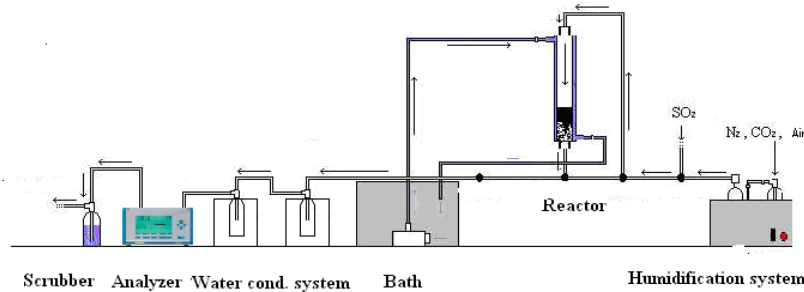
Figure 1: Experimental setup for desulfurization post combustion

For the desulfurization post combustion with the reactivated sorbents, approximately 1g of the sorbent was used and the reaction took place in the experimental setup of the Figure 1. The experimental conditions were: 5000 ppm SO_2 in the flue gas, 55 % of relative humidity and a temperature of 58º C in the reactor. The concentration of SO_2 after the reaction was continuously monitored with a personal computer equipped with a NGA 2000 MLT1 Emerson win control software; the breakthrough curves of SO_2 concentration in the gas stream leaving the reactor were plotted. When the reaction time was over (controlled by the breakthrough curves), the reacted sorbent was sieved to separate the reacted sorbent from the sand.

In this post combustion desulfurization, the ability to capture the SO_2 was calculated in two different ways: a) with the NGA analyser b) by submitting the sorbent, after capturing the SO_2, to a thermogravimetric analysis as has been explained previously.

3. Results

3.1 Calcium conversion values for desulfurization during combustion:

Calcium conversion values quantified as mol SO_2 captured / mol Ca in the sorbent were obtained in this case by thermogravimetric analysis of the <u>solids</u> (ashes obtained in the furnace by combustion of sludge/$CaCO_3$ mixtures), considering the mass loss between 850 and 1200º C due to the decomposition of the $CaSO_4$ in SO_3 and CaO. Next equation was used to obtain the value of mole SO_2/mol Ca:

$$\frac{\left(\dfrac{\% \, SO_3}{100} - \dfrac{\% \, of \, ash}{100} * \dfrac{g \, of \, ash}{g \, of \, sorbent} \right) \dfrac{1 \, mole \, SO_3}{80 \, grams \, SO_3}}{\dfrac{moles \, of \, calcium}{grams \, of \, sorbent}} \tag{1}$$

In this equation, value of *% SO_3* was calculated from the T.G. curve of the solid or sorbent (ashes obtained in the furnace by combustion of sludge/$CaCO_3$ mixtures) after the desulfurization reaction and *% of ash*, was calculated from T.G. curve of the ash obtained without $CaCO_3$ considering in both cases, the mass loss between 850 and

1200º C. Figure 2 shows the thermogravimetric curve of ashes without $CaCO_3$ added. From this curve a value of % of ash = 2.468 was obtained.

Operating in this way, only the SO_2 captured with the calcium base added as $CaCO_3$, is considered to obtain the calcium conversion as that is the calcium relevant from an economical point of view.
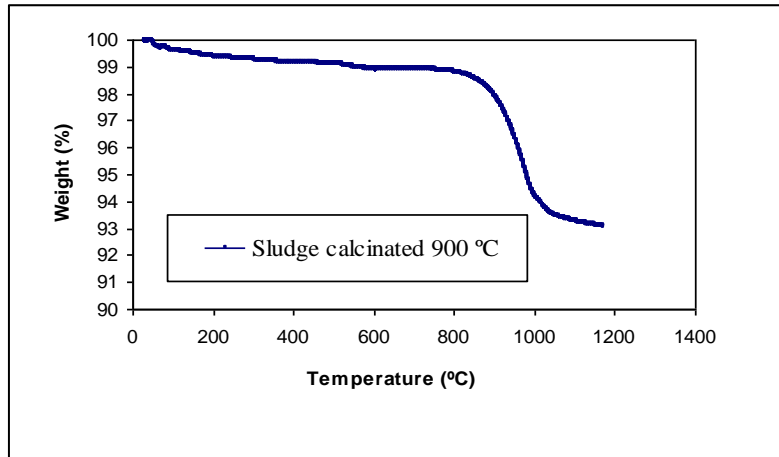

Figure 2: Thermogravimetric curve of the ashes of the sludge ignited at 900º C

To calculate the denominator in equation (1), it is necessary to know the behaviour of sludge in the combustion process. Data of this behaviour are presented elsewere (Renedo et al., 2010). For the ashes obtained by combustion of the mixture 10 sludge /1 $CaCO_3$, calcium conversion value was obtained as follows:

moles SO_2 captured /mol of calcium =

$$\frac{\left(\dfrac{6.678}{100} - \dfrac{2.468}{100} * \dfrac{10}{11}\right) \dfrac{1\,mole\,SO_3}{80\,grams\,SO_3}}{\dfrac{98\,g\,pure\,CaCO_3}{100\,g\,comm.\,CaCO_3} \times \dfrac{1\,mole\,CaCO_3}{100\,g\,pure\,CaCO_3} \times \dfrac{1\,g\,of\,comm.\,CaCO_3}{11\,grams\,sludge} \times \dfrac{100\,grams\,sludge}{52.49\,grams\,of\,sorbent}}$$

x 100 = 32.66 %

Table 1 shows the results obtained for 10/1 and 10/10 sludge/$CaCO_3$ ratios.

Table 1 Desulfurization during combustion for 10/1 or 10/10 sludge /$CaCO_3$ ratios.

Desulfurization during sludge combustion. (900º C.)	Temperature /time	(Mol SO_2 captured/mol of added Ca) x 100.
10g dry sludge + 1g $CaCO_3$	900 ºC, 2 hours	32.66
10g dry sludge + 10g $CaCO_3$	900 ºC, 2 hours	4.8

Results show that not all the $CaCO_3$ added to the sludge is used to retain the SO_2 mainly when the sludge/$CaCO_3$ ratio was 10/10. This result can be explained considering that most of the salt added in this mixture, remains as calcium carbonate and low amounts of the desulfurant base, CaO, are present as has been proved by thermogravimetric analysis of the ashes. When the sludge/$CaCO_3$ ratio is 10/1 the SO_2 captured is higher (per mole of added calcium); that means that the $CaCO_3$ is calcinated in higher percentage and the CaO can capture more SO_2. This behaviour can be explained considering the difficulties of the CO_2 diffusion through the solids that impede the progress of the calcination.

3.2 Calcium conversion values for desulfurization post combustion with the reactivated ashes.

As Table 2 shows different ways of reactivation of the ashes were essayed. Sorbent number 5 was obtained by hydration of the ashes formed in the oven from the sludge without $CaCO_3$ and new CaO at a 10/1 ashes/CaO ratio. The rest of the sorbents were obtained reactivating the ashes by hydration without adding CaO.

Table 2 Calcium conversion, as mol SO_2 captured/mol Ca, obtained from T.G. data for the reactivated sorbents in the desulfurization at low temperature.

Desulfurization at 55° C with reactivated ash. (Reuse of ashes)	Reactivated sorbent number	Reactivation conditions	(Mol SO_2 captured / mol of added Ca) x 100 From T.G. data
Ashes from (10g dry sludge + 1g $CaCO_3$) +10 mL H_2O	1	90 °C, 7 h	16.3
Ashes from (10g dry sludge + 10g $CaCO_3$)+10 mL H_2O	2	90 °C, 7 h	3.5
Ashes from (10g dry sludge + 1g $CaCO_3$)+ 10 mL H_2O	3	Room temperature 15 min	19.1
Ashes from (10g dry sludge + 10g $CaCO_3$) +10 mL H_2O	4	Room temperature 15 min	3.1
10g ashes +1g CaO+ 7ml H_2O	5	90 °C , 7 h	55

As the post combustion desulfurization process took place in the experimental set up shown in Figure 1 with a continuous analyser of the SO_2 in the effluent gas, results of calcium conversion were also obtained by using the breakthrough curves of SO_2 For sorbent 5, the value of mol SO_2 captured/mole of Ca obtained by using the breakthrough curves was 45.6%. From TG data, considering the mass loss within 850 and 1300 ° C and subtracting the mass loss coming from the same solid before being submitted to the flue gas, the calcium conversion for sorbent 5 was 55 %. For the rest of the sorbents, 1, 2, 3 and 4, the *moles Ca /g of sorbent* was obtained subtracting, from the calcium base added in the furnace, the amount of the base used to capture the SO_2 during the combustion (this amount is obtained from the value of the conversion during the

combustion). Only the remaining calcium base was considered as it is the base that can retain SO_2 at low temperature (55 ºC). Results of Table 2 shows, as could be expected, that if new calcium base is added to the ash in the reactivation process, the SO_2 captured is higher than if calcium base is not added. But, when the aim of the experiment is to simulate the reuse, the normal way is to reactivate the solid without adding new base as it was made with sorbents 1, 2, 3 and 4. Results for these sorbents show that, the main factor related to the ability to capture SO_2 after reactivation is, as in the desulfurization during combustion, the dry sludge / $CaCO_3$ ratio. When this ratio is 10/1, the moles of SO_2 captured /mol calcium are similar each other, 16.3 or 19.1, independently of the reactivation conditions. With sorbents prepared at a 10/ 10 ratio, the SO_2 captured was much lower independently of the reactivation process.

From the values of capture of SO_2 during the combustion and post combustion (after having reactivated the solid), it can be concluded that the best results are obtained, adding $CaCO_3$, at a dry sludge / $CaCO_3$ ratio of 10/1 and reactivating by hydration at room temperature. Reactivation at 90º C during 7 hours do not produce better results, meaning that hydration of CaO, that occurs easily at room temperature, is the unique reaction that take place in the process.

4. Conclusions

The SO_2 capture during the calcination at 900º C is much higher at the 10 sludge/1 $CaCO_3$ ratio. The best desulfurization behaviour, at low temperature, was found with the sorbent coming from the ashes obtained from the mixture 10 sludge /1 $CaCO_3$ and reactivated by hydration at room temperature.

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