Short communication

Regenerable CaO sorbents for SO_2 retention: carbonaceous versus inorganic dispersants[☆]

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Abstract

In this study, the behaviour of different activated carbons and some inorganic solids (alumina, silica, titania, magnesia and silicon carbide) as dispersants for $Ca(OH)_2$-derived CaO under two cycles of SO_2 retention at 300 °C, is analysed. Before performing the second SO_2 adsorption, a regeneration treatment in N_2 at 880 °C is carried out. During the first retention of SO_2, no influence of the dispersant was appreciated, being CaO the only phase responsible of SO_2 capture. However, during the second SO_2 adsorption the nature of the dispersants is important. Thus, comparing the behaviour of the inorganic solids with that exhibited by the activated carbons, it is observed that the activity loss, after the regeneration treatment, was significantly reduced when the activated carbons were used, especially at high dispersant content. The most effective dispersants were found to be those with meso and macroporosity which prevent the CaO (particle size of about 5 nm) sinterisation–agglomeration. This feature was exhibited by the activated carbons chosen. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium sorbent; SO_2 retention; Regeneration; Carbonaceous dispersant; Inorganic dispersant

1. Introduction

SO_2 emission control in coal-fired power plants by means of injection of calcium-based sorbents is being widely studied at low (in-duct injection, below 150 °C) and high temperature (furnace injection, 700–1200 °C) as an alternative to wet desulphurisation processes for existing units [1,2]. Nevertheless, the study of the reaction between $Ca(OH)_2$ and the SO_2 in the flue gas at medium temperature (economiser injection) is less developed [1,3]. Calcium hydroxide is a potential reagent for SO_2 control in the medium temperature range (300–600 °C), where the reaction rate should be very fast allowing higher conversions than furnace injection [1,3–5].

According to previous XRD, TG, TPR, isothermal reaction, TPD after sulphation and in situ infrared studies, CaO reacts with SO_2 to form $CaSO_3$ below 400 °C, both in the presence and absence of oxygen [6–11]. Interestingly, calcium sulphite thermally decomposes to SO_2 and CaO above 700 °C [7–11]. Consequently, SO_2 retention by CaO to form $CaSO_3$ is theoretically reversible, in line with the expected future preferences for regenerative technologies [12]. Unfortunately, this theoretical reversibility presents some problems as it has been reported in previous works [8,10,11,13]. Thus, although an important amount of SO_2 can be retained by CaO at temperatures around 300 °C, (as high as 250 mg/g), a dramatic loss in a subsequent SO_2 retention step is observed. In earlier works [8,10,11,13], the possible causes of activity loss were studied: (i) sinterisation–agglomeration of CaO during the thermal treatment due to $CaSO_3$ presence, (ii) $CaSO_3$ desproportionation to $CaSO_4$ and CaS and (iii) $CaSO_3$ reduction to calcium sulphide, (the latter only feasible when carbonaceous materials are used as dispersants). It was found that for $Ca(OH)_2$-derived CaO, the loss in activity is mainly due to a sinterisation–agglomeration process [8]. CaO dispersion can be a promising route to diminish this loss of active surface area [8,10]. Therefore, the goal of this work is to deepen into the study of the use of carbonaceous as well as inorganic dispersants to prepare different CaO-based sorbents and to

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test their behaviour under two cycles of SO_2 retention (first SO_2 adsorption–regeneration treatment in N_2- second SO_2 adsorption).

2. Experimental

2.1. Samples

Commercially available $Ca(OH)_2$ (PANREAC, 95% weight purity) was used as CaO precursor. Samples, with $Ca(OH)_2$ contents ranging from 20 to 90% in w/w, were prepared by physical mixture with different dispersants. In brief, this method consists of intimately mixing the dispersant and the $Ca(OH)_2$, both finely powdered, in a commercial grinder Herzog HSM100.

Two sets of dispersing agents were tested: inorganic (commercially available alumina, silica, magnesia, titania and silicon carbide) and carbonaceous materials (a commercial activated carbon supplied by Westvaco and two activated carbons prepared in our laboratory under steam activation at 800 °C: A3S10 and A3S30 (10 and 30% of burn-off, respectively)). The meso and the macroporosity of some of the dispersants were estimated by means of a mercury porosimeter Carlo Erba 2000.

2.2. SO_2 retention experiments

Isothermal SO_2 retention experiments were performed at 300 °C using a reactive gas consisting of a SO_2/N_2 mixture (0.2 vol% SO_2). The experimental procedure was as follows: (i) the sample was heated in N_2 up to 450 °C for 10 min (20 °C/min) with the purpose to decompose the calcium hydroxide present in the samples into calcium oxide; (ii) the sample was then cooled at 20 °C/min to the reaction temperature (300 °C); (iii) the reaction mixture was put in contact with the sample until saturation of the sorbent; (iv) the thus-treated sample was heated at 20 °C/min, in N_2, up to 880 °C for 10 min, with the purpose to regenerate the sorbent and (v) the treated sample was again put in contact with the reactive mixture at 300 °C until saturation of the sorbent. This set of experiments was performed by using two types of experimental devices:

(a) A thermobalance (Stanton–Redcroft Series 780) in which 10 mg of sample were exposed to a gas flow of 90 ml/min, (0.2 vol% SO_2/5% O_2 in N_2).
(b) A tubular quartz reactor coupled to different NDIR-UV gas analysers (Fisher–Rosemont, Binos series 100, 1001 and 1004) for the quantification of SO_2, O_2, CO and CO_2. The sample mass and the gas flow used were 200 mg and 620 ml/min, respectively.
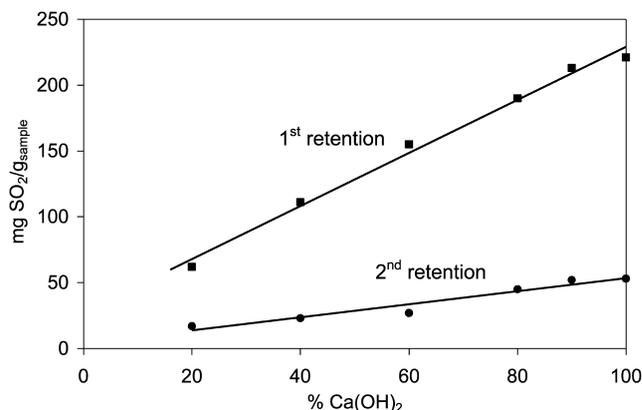

Fig. 1. SO_2 retention capacity of $Ca(OH)_2$-derived CaO with different contents of Al_2O_3 for the first and the second cycles.

3. Results and discussion

3.1. SO_2 retention by sorbents prepared with inorganic dispersants

Fig. 1 shows the amounts of SO_2 retained by a series of $CaO–Al_2O_3$ samples with different $Ca(OH)_2$ contents. It compiles the results before and after the regeneration step, that will be named *first retention capacity* and *second retention capacity*, respectively. The *retention capacity* increases linearly with the $Ca(OH)_2$ content. Moreover, the retention capacity of the samples decreases significantly after regeneration. This behaviour indicates that CaO is the only active phase responsible of SO_2 capture, as expected.

As pointed out in Section 1, the *activity loss* is the main adverse consequence of the regeneration step [8,11]. This parameter was defined as follows:

$$\text{Activity loss}(\%) = 100 - \frac{\text{mg } SO_{2(\text{2nd retention})}}{\text{mg } SO_{2(\text{1st retention})}} \times 100 \quad (1)$$

Table 1 shows that the activity loss of the sorbents prepared using alumina as dispersant does not depend on the CaO content, being more or less constant (approximately 76%). Thus, the alumina studied is not a suitable dispersant and does not reduce the activity loss after a second retention in comparison with undispersed-CaO, (100% $Ca(OH)_2$).

Table 2 illustrates the first and second retention capacities (calculated as milligrams of SO_2 retained per gram of sorbent), the *calcium efficiency* (calculated as mole

Table 1
Activity losses deduced from samples prepared with Al_2O_3 as dispersant

Sample	Activity loss (%)
Al_2O_3 80% + $Ca(OH)_2$ 20%	73
Al_2O_3 60% + $Ca(OH)_2$ 40%	79
Al_2O_3 40% + $Ca(OH)_2$ 60%	82
Al_2O_3 20% + $Ca(OH)_2$ 80%	76
Al_2O_3 10% + $Ca(OH)_2$ 90%	76
Al_2O_3 0% + $Ca(OH)_2$ 100%	76

Table 2
SO$_2$ retention capacities (first and second), calcium efficiency and activity loss of the sorbents prepared with a 20% in w/w of each inorganic dispersant

Sample	First retention (mg SO$_2$/g)	Calcium efficiency (mol SO$_2$/mol CaO)	Second retention (mg SO$_2$/g)	Activity loss (%)
Al$_2$O$_3$ 20% + Ca(OH)$_2$ 80%	189.6	0.27	45.2	76
SiO$_2$ 20% + Ca(OH)$_2$ 80%	199.5	0.29	35.5	82
MgO 20% + Ca(OH)$_2$ 80%	196.4	0.28	42.9	78
TiO$_2$ 20% + Ca(OH)$_2$ 80%	202.8	0.29	35.5	82
SiC 20% + Ca(OH)$_2$ 80%	212.9	0.27	59.9	68

SO$_2$ retained per mole CaO in the sorbents) and the activity loss after regeneration of the sorbents prepared with a fixed amount of each inorganic dispersant (20% in w/w) where SO$_2$ retention capacity is still high (≈ 200 mg SO$_2$/g). The calcium efficiencies estimated are constant whatever the inorganic dispersant used, showing the useless of an inorganic dispersant, independently on their different chemical nature. In all the cases, the loss in activity remains high (around 70–80%).

3.2. SO$_2$ retention by sorbents prepared with carbonaceous dispersants

Carbonaceous materials can be prepared with a high surface area and external roughness [14] allowing a high dispersing effect. Three activated carbons were selected for this study, A3S10 (BET surface area = 636 m^2/g), A3S30 (BET surface area = 714 m^2/g) and Westcavo (BET surface area = 1100 m^2/g).

Fig. 2 collects the first retention capacity, corresponding to the set of samples prepared, as a function of their Ca(OH)$_2$ contents. No significant differences were appreciated between samples prepared with inorganic or carbonaceous dispersants, which corroborates that CaO is the only active phase for SO$_2$ capture. From a practical point of view, it is important to highlight that the experiments performed by using the multi-gas analysers, that allows to follow CO and CO$_2$ evolution, show no carbon gasification (less than 0.5%) neither during SO$_2$ retention nor thermal regeneration in N$_2$. Fig. 2 clearly shows that, if the samples are not
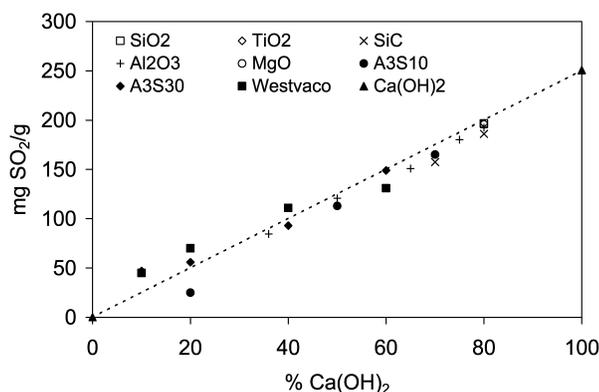
'reused', the use of dispersants is negative and that the best results are observed with pure Ca(OH)$_2$.

Fig. 3 includes the activity loss obtained when different Ca(OH)$_2$ contents were dispersed onto the three activated carbons studied. For comparative purposes, the alumina series was also collected. Opposite to the trend shown by alumina, the sorbents prepared with carbonaceous materials as dispersants exhibit a similar improvement of activity during the second retention, mainly at low Ca(OH)$_2$ content, even taking into account their different surface area (600–1100 m^2/g). This finding supports the hypotheses defended in previous publications [8,10] about a possible route to decrease the high activity loss of pure Ca(OH)$_2$ would be the dispersion of this compound onto a proper dispersant.

Concerning the subsequent cycles of SO$_2$ retention, the activity losses are much lower in a third SO$_2$ retention, (about 0–6% of activity loss with regard to the second retention) for the set of samples studied with the activated carbons as dispersants.

In order to evaluate the influence of the surface texture of the different dispersants on the activity losses of the sorbents, those were analysed by mercury porosimetry. As an example, Fig. 4 collects the pore size distribution (pore radius from 3.8 to 7500 nm) of an inorganic dispersant (alumina) and the three activated carbons. Whereas the alumina shows almost no porosity in the range studied, the activated carbons exhibit high pore volume at pore sizes from 3.8 to 20 nm. Additionally, Table 3 compiles the pore volume of the dispersants studied, estimated from Hg-porosimetry (from pore radius higher than 5 nm). Only the carbonaceous samples present a significant meso and macropore volume whereas the alumina is mainly a non porous solid in the range studied. From these results and
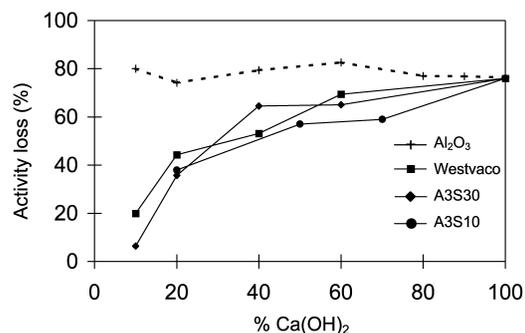

Fig. 2. First SO$_2$ retention capacity versus Ca(OH)$_2$ content for the set of samples studied.

Fig. 3. Activity loss of the sorbents prepared with carbonaceous materials and Al$_2$O$_3$ as dispersants as a function of the Ca(OH)$_2$ content.
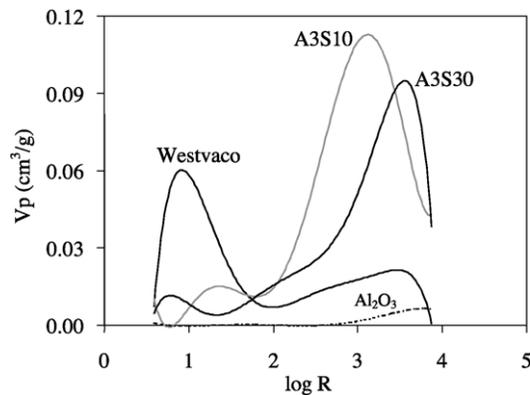
Fig. 4. Pore size distribution of some of the dispersants used obtained from mercury porosimetry.

Table 3
Pore volume for different dispersants deduced from mercury porosimetry

Dispersant	V^a (cm^3/g)
Westvaco	0.76
A3S10	1.19
A3S30	0.79
Al_2O_3	0.02

[a] For pore radius higher than 5 nm.

those shown in Fig. 3, we can conclude that those dispersants with a rough surface are the most effective. This observation is in agreement with the fact that rough dispersants (carbonaceous materials) can diminish the migration of the CaO particles (average particle size about 5 nm, estimated by CO_2 chemisorption at 573 K) [8], and subsequent sinterisation, better than the smooth ones (inorganic compounds).

In earlier studies [10,12], the CaO dispersion onto activated carbons (by means of the ion-exchange and impregnation techniques) was analysed in order to increase SO_2 retention with regard to unsupported-CaO. The main advantages of the physical mixture, here reported, against ion-exchange or impregnation are as follows:

(i) Higher calcium loading: the maximum amount of calcium that can be introduced on samples by impregnation is about 10–15% in weight.
(ii) Simplicity of the process.
(iii) No carbon gasification can be quantified neither during SO_2 retention at 300 °C in the presence of oxygen, nor during the regeneration treatment in N_2. These phenomena were observed in previous works carried out with Ca-impregnated activated carbons, where an important carbon gasification was observed during the SO_2 retention (due to O_2 consumption).

4. Conclusions

As conclusions, $Ca(OH)_2$-derived CaO sorbents dispersed both onto inorganic and carbonaceous compounds present similar first SO_2 retention capacity at 300 °C. The dispersants, which do not retain SO_2, decrease the retention capacity of the samples, which is a function of the calcium content of the sorbents. Nevertheless, after the regeneration step in N_2 at 880 °C, the use of dispersant can be important in the case of activated carbons because the sorbents prepared from carbonaceous dispersants exhibit a lower activity loss for a second SO_2 retention, mainly at low calcium loadings. The better dispersing effect of the carbonaceous materials seems to be related to the presence of porosity with pore sizes higher than the CaO particle size (about 5 nm), thus avoiding the sinterisation–agglomeration of the calcium oxide particles.

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