Hydration Products of FBC Нastes as SO₂ Sorbent: Comparison between Calcium Hydroxide and Ettringite

Fabio Montagnaro¹, Marianna Nobili², Piero Salatino³, Antonio Telesca², Gian Lorenzo Valenti²

1. Dipartimento di Chimica - Università degli Studi Federico II, Naples - ITALY
2. Dipartimento di Ingegneria e Fisica dell’Ambiente - Università degli Studi della Basilicata, Potenza - ITALY
3. Dipartimento di Ingegneria Chimica - Università degli Studi Federico II, Naples - ITALY

1. Overview

Fluidized bed combustion (FBC) residues are characterized by a poor pozzolanic activity and show exothermic and expansive phenomena upon hydration. Therefore, they are generally unsuitable for recycling in the traditional fields for combustion wastes such as in the cement and concrete industries. Application of water reactivated FBC residues as sorbent for in situ SO₂ capture, upon their reinjection in the fluidized bed combustor, has long been considered a viable alternative to other uses, relying on the waste ability to quantitatively yield Ca(OH)₂ [1,2].

In addition to Ca(OH)₂, other hydration products such as calcium silicate hydrates, calcium aluminate hydrates and calcium sulphaaluminate hydrates are generated: so far, little attention has been paid to their ability to act as sorbents during in situ FBC desulphurization processes [3]. In particular, there is lack of information about the behaviour of ettringite, a calcium trisulphoaluminate hydrate (3CaO·Al₂O₃·3CaSO₄·32H₂O) which can be formed to an extent mostly dependent on the composition of the residue and on the hydration conditions [4]. Ettringite is worthy of consideration because of its low thermal stability and ability to yield, upon FBC dehydration, CaO available for SO₂ capture [5-7].

Substantial changes in the particle size distribution of sorbents can be brought about by particle fragmentation/attrition during FBC sulphation. These comminution phenomena determine the generation of both fine particulates of elutriable size and of coarse non-elutriable fragments. While the occurrence and extent of these phenomena for commonly-employed limestone-based sorbents have been the subject of several studies [8,9], the investigation on sorbents other than limestone (such as Ca(OH)₂ and ettringite) has received comparatively little attention [6,7].

Aim of this paper is to compare the behaviour of Ca(OH)₂ and ettringite as SO₂ sorbents for FBC desulphurization, by investigating their sulphur capture ability and attrition/fragmentation tendency during experiments conducted in a lab-scale FB reactor. Particular emphasis is given to the study of the pore size distribution and of the porosimetric texture changes for both sorbents upon dehydration and subsequent sulphation.

2. Experimental

2.1. Sorbents

Synthetic ettringite (ET) was prepared following the Mylius procedure [10], thus employing solutions of Ca(OH)₂, CaSO₄·2H₂O and Al₂(SO₄)₃·18H₂O. Synthetic calcium hydroxide (CH) was obtained by pure CaO hydration. Both sorbents were sieved in the particle size range 0.4-0.6mm, which was chosen for all the experimental tests. X-ray diffraction, differential thermal and thermogravimetric analyses conducted on both ET and
CH indicated that both sorbents had a high purity degree. Moreover, ET and CH particles were submitted to mercury intrusion porosimetric analysis.

2.2. Dehydration and sulphation tests

ET and CH were fully dehydrated (ET-D and CH-D) in an electric oven at 850°C, and then submitted to porosimetric investigation.

Sulphation tests of either ET-D or CH-D were conducted in a stainless steel bench-scale (40mm ID, 1m high) atmospheric bubbling FB reactor, electrically heated [2]. The bed material consisted of a batch of 10g of sorbent + 150g of 0.85-1mm silica sand. The operating temperature was 850°C, the fluidizing gas superficial velocity was 0.8m/s, the fluidizing gas composition was 1800ppmv SO$_2$ + 17.5%v O$_2$ + N$_2$. For each sulphation test, flue gases were continuously sampled in order to monitor the outlet SO$_2$ molar flow rate, thus allowing to obtain the degree of calcium conversion $X_{Ca}$ as a function of sulphation time:

$$X_{Ca}(t) = \frac{\int_0^t [F_{SO_2}^{in} - F_{SO_2}^{out}(t)]dt}{n_{CaO}}$$

where $F_{SO_2}^{in}$ and $F_{SO_2}^{out}(t)$ are the molar flow rates of SO$_2$ fed to the reactor and measured at the exhaust, respectively, while $n_{CaO}$ is the number of CaO moles of the sorbent fed to the reactor and available for sulphation. Moreover, the sorbent fines elutriation rate during sulphation tests was calculated by means of a two-exit reactor head designed to convey flue gases into either of two sintered brass filters. After the full exhaustion of the sorbents, dehydrated-sulphated ettringite (ET-DS) and calcium hydroxide (CH-DS) in-bed particles were retrieved and subjected to particle size distribution analysis by laser granulometry, in order to investigate the sorbents fragmentation behaviour. Finally, ET-DS and CH-DS particles were submitted to porosimetric investigation.

3. Results

3.1. Dehydration of ettringite (ET-D) and calcium hydroxide (CH-D)

Before sulphation tests, ET and CH were dehydrated in order to investigate their pore size distributions. This is particularly important since, upon FBC sulphation, dehydration has a much shorter time-scale than sulphur uptake: hence, it is the porosimetric texture of dehydrated sorbents, rather than that of the parent ones, to be encountered by the SO$_2$ molecules during the gas-solid desulphurization reaction.

Dehydration/thermal decomposition of ET and CH yields a remarkable increase in the overall porosity (1275mm$^3$/g for ET, 1559mm$^3$/g for ET-D; 358mm$^3$/g for CH, 683mm$^3$/g for CH-D). Figures 1a and 1b show the absolute and cumulative pore size distribution, respectively, for the two dehydrated sorbents. It can be observed that in the intermediate pore radius range of 10-200nm CH-D shows a greater porosity, while particularly noticeable is the difference between the porosity of ET-D and CH-D for pores of radius>200nm. Thus, the cumulative pore size distributions intersect each other at a pore radius of about 1000nm. It should be recalled here that: i) both the finer/intermediate pores -more reactive- and the greater pores -more spacious- may play a role in the SO$_2$ uptake [11]; ii) the overall porosities of ET-D and CH-D are well greater than those encountered when dealing with typical calcined commercial limestones [2].
3.2. Sulphation of dehydrated ettringite (ET-DS) and dehydrated calcium hydroxide (CH-DS)

Figure 2a reports the $X_{Ca}(t)$ trends during FB sulphation tests of ET-D and CH-D. It can be observed that the calcium oxides deriving from the thermal decomposition of ET and CH have comparable reactivity, with ultimate degrees of calcium conversion of nearly 80%. The longer exhaustion time-scale for CH-DS is to be ascribed to the circumstance that, when feeding to the reactor an equal mass of ET-D and CH-D, the latter has a quadruple free CaO mass content. Both sorbents show a much greater sulphur uptake when compared with commercial limestones, whose typical ultimate degrees of calcium conversion seldom exceed 30-40%.

Figure 2b shows the fines elutriation rates obtained during FB sulphation tests of ET-D and CH-D. The elutriation rate decreases with time following a trend qualitatively similar to those observed during limestones sulphation [2,8,9]: in the early stage of the test, both thermal stress and removal of surface asperities (particles rounding-off) are relevant; as sulphation proceeds, the elutriation rate decreases due to the particle hardening associated
with CaO conversion to CaSO$_4$. Upon sulphation, ET-D particles show a greater elutriation tendency: about 30% by mass of the sorbent feed was retrieved as elutriated fines, compared to 5% for CH-D. This should be ascribed to the softer nature of ET-D particles, and to the fact that ET-D also contains Al-based phases which do not take part in the sulphation process, thus not contributing to the particle hardening. The impact of attrition on the performance of the sorbents should be considered in the light of two conflicting effects. On one hand, attrited fines are characterized by shorter residence times in the reactor when compared with the parent particles, and this may negatively affect calcium conversion. On the other hand, due to its smaller size attrited material is characterized by better conversion rates when compared with the mother particles. Whether and how the two effects balance each other cannot be established on a priori basis, without considering important design and operational parameters of the FB process.

*Figures 3a and 3b* show the absolute and cumulative particle size distributions, respectively, for the two sorbents retrieved from the bed after sulphation tests. The in-bed fragmentation of ET-D during sulphation is greater than that of CH-D: the two mean Sauter diameters are 0.367mm (ET-DS) and 0.457mm (CH-DS). In addition, the debris fraction (i.e., the percentage of in-bed fragments whose size falls below 0.4mm, the lower limit of the feed size interval) is 62% for ET-DS, 30% for CH-DS. Fragments <0.2mm in size are easily elutriable and therefore almost absent in the bed material. These data are in accordance with the elutriation rate results, highlighting the greater ettringite tendency to undergo comminution phenomena. Also when considering the in-bed fragmentation results it should be reminded the better reactivity shown by the fragmented material smaller in size.

CH-DS shows a negligible porosity throughout the whole pore size range investigated. Data for ET-DS, compared with those previously reported for ET-D, are shown in *Figure 4a* (on an absolute basis) and *Figure 4b* (on a cumulative basis). For all the pore radius ranges but 150-200nm, sulphation induces a remarkable porosity reduction. The overall porosity decreases from 1559mm$^3$/g (ET-D) to 579mm$^3$/g (ET-DS). While the sulphur capture ability of different sorbents is certainly related to their chemical reactivity, nonetheless the physical role played by the particles porous texture must be taken into consideration. In this context, the similar reactivity shown by the calcium oxides deriving from the thermal decomposition...
of ettringite and calcium hydroxide could be partly explained by considering that, even if not all the dehydrated ettringite porosity is exploited (differently from dehydrated calcium hydroxide), its >200nm porosity is greater than that of dehydrated calcium hydroxide. Thus, these results highlight the role that the larger pores, along with the finer ones, play in determining the physical tendency of a sorbent to capture SO$_2$. Of course, in this context, both the pores morphology [12] and the contribution given by inactive phases in the sulphur capture to the ettringite porosity, together with the occurrence and extent of attrition/fragmentation phenomena, should be borne in mind.

![Fig. 4a (left) Absolute pore size distribution for ET-D and ET-DS.](image1)
![Fig. 4b (right) Cumulative pore size distribution for ET-D and ET-DS.](image2)

4. Concluding remarks

Synthetic preparations of Ca(OH)$_2$ and ettringite were investigated in order to compare their degree of calcium conversion and attrition/fragmentation propensity upon sulphation in fluidized bed combustion processes.

Both SO$_2$ sorbents were first dehydrated to study the porosimetric changes occurred in comparison to the raw materials. It was found that the overall porosity generally increases, showing a more pronounced effect for the finer/intermediate pores in calcium hydroxide and for the larger ones in ettringite. Both the overall porosities were well greater than those encountered when dealing with typical calcined commercial limestones.

Upon fluidized bed sulphation of dehydrated ettringite and calcium hydroxide, the two materials exhibited a comparable degree of calcium conversion (nearly 80%, much greater than the values obtainable by means of commercial limestones). As far as elutriation tendency is concerned, ettringite showed a greater propensity to undergo attrition due to its softness and to the presence of Al-based phases not contributing to the particle hardening upon sulphation. Also the particle size distribution data confirmed the greater ettringite tendency to experience comminution phenomena. For calcium hydroxide, sulphation caused a complete pore plugging, whereas the available porosity of ettringite was only partly exploited.

Finally, the results obtained highlighted that the physical role played by the particles porous texture must be taken into consideration when considering the sorbent reactivity, together with the chemical reactivity as well as the occurrence and the extent of attrition/fragmentation phenomena.
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6. References