The Role of Ettringite in the Re-use of Hydrated Fly Ash from Fluidized Bed Combustion as Sulphur Sorbent

G. Bernardo, F. Montagnaro, P. Salatino, A. Telesca, G. L. Valenti

Dipartimento di Ingegneria e Fisica dell’Ambiente
Università degli Studi della Basilicata, Potenza - Italy
Dipartimento di Chimica, Università degli Studi Federico II, Naples - Italy
Dipartimento di Ingegneria Chimica, Università degli Studi Federico II, Naples - Italy

INTRODUCTION

Fluidized Bed Combustion (FBC) waste contains both a fuel ash with a poor pozzolanic activity and an exhausted SO₂ sorbent composed by particles of CaSO₄ and unreacted CaO responsible for exothermal and expansive phenomena upon hydration. Hence FBC waste is generally unsuitable for applications in traditional fields of utilization such as ordinary cement and concrete industries [1].

Among the proposed reuses, it is worthy of consideration the reinjection of FBC waste into the combustor after a hydration-induced reactivation process aimed at exploiting its desulphurization potential. This is mainly related to the waste ability to form calcium hydroxide, as highlighted by Shearer et al. [2], Couturier et al. [3], Laursen et al. [4], Scala et al. [5] and Jia et al. [6].

However the reactivation process may generate other hydration products able to enhance the sorbent capacity, such as ettringite, a hexacalcium trisulphoaluminate hydrate (3CaO·Al₂O₃·3CaSO₄·32H₂O). The sulphation behaviour of synthesized ettringite was investigated in a thermogravimetric analyzer [7] and in a lab-scale FB reactor [8]: in both cases it has been found that the products of ettringite decomposition show a sulphur uptake ability much higher than that of a commercial limestone operating under the same experimental conditions.

Substantial changes in the sorbent particle size distribution can be brought about by particle attrition/fragmentation. As highlighted by Scala et al. [9] and Montagnaro et al. [8], comminution phenomena may significantly affect particle sulphation and elutriation: mutual effects of sulphation and attrition were also recognized, resulting into a progressively reduced attrition caused by the build-up of a hard sulphated shell.

A kinetic study is in progress with the purpose of individuating the optimal curing temperatures and times at which ettringite-rich materials can be formed by liquid-phase hydration of FBC wastes. In this paper a residue coming from an industrial FB boiler, reactivated by a hydration treatment carried out for 48 h at 70°C, has been investigated at a laboratory scale. Its performance as a sorbent under simulated combustion/desulphurization conditions has been evaluated in terms of sulphur uptake ability and attrition/fragmentation behaviour.

EXPERIMENTAL

The reactivated material was generated by hydration of a previously investigated FBC fly ash [10] with a large water/solid weight ratio (w/s=100). At the end of the curing in a thermostatic bath, the samples were vacuum filtered, ground under acetone, dried with ether in an agate mortar and finally stored in a desiccator ensuring protection against water and carbon dioxide attack. Calcination, sulphation and attrition/fragmentation tests on the sorbent material were carried out in a stainless steel atmospheric bubbling FB reactor of laboratory
scale (40 mm ID and 1 m high), electrically heated [9], having a two-exit head designed to convey the flue gases through either of two sintered brass filters (filtration efficiency=100% for >10 µm-particles). The alternate use of such filters enabled a time-resolved capture of the elutriated fines at the exhaust. The flue gases were rapidly cooled down and continuously sampled for SO$_2$ concentration measurements by a nondispersive infrared analyzer on line. The SO$_2$ concentration signals in flue gases were logged on a PC at a sampling rate of 1 Hz.

The procedures before the start of the calcination test were the following: 1) the reactor was heated up to 850°C; 2) a silica sand bed was charged and fluidized with air; 3) a batch of sorbent was added to the bed. The operating conditions were: a) bed material, sorbent (10 g) + silica sand (150 g); b) sorbent size range, 0.425-0.600 mm; c) sand size range, 0.850-1.000 mm; d) process time, 20 minutes; e) fluidizing gas, air; f) air superficial velocity, 0.8 m/s. The choice of a particle size range for the sorbent different from that for the sand made easy its retrieval. The operating conditions employed for the sulphation test were the same as those for the calcination test, except for the process time (100 minutes) and the composition of the fluidizing gas (1800 ppmv SO$_2$, 8.5% O$_2$, balance N$_2$). The SO$_2$ concentration values measured at the exhaust were worked out to calculate the instantaneous sulphur uptake efficiency

$$\eta(t) = \frac{F^{in}_{SO_2} - F^{out}_{SO_2}(t)}{F^{in}_{SO_2}}$$  \hspace{1cm} (1)$$

and the instantaneous degree of calcium conversion

$$X_{Ca}(t) = \int_0^t \left[ F^{in}_{SO_2} - F^{out}_{SO_2}(t) \right] dt$$ \hspace{1cm} (2)

where $F^{in}_{SO_2}$ and $F^{out}_{SO_2}(t)$ are the molar rates of SO$_2$ fed to the reactor and in the exhaust gas, respectively; $n_{CaO}$ are the moles of free calcium oxide generated upon sorbent dehydration/calcination and deriving from the lime combined into ettringite, the contribution arising from other calcium compounds being neglected [7]. The extent of SO$_2$ oxidation to SO$_3$ was calculated with the aid of blank tests according to Scala et al. [9].

During the sulphation, the time-resolved attrition/fragmentation rate of sorbent particles was determined by the collection of the elutriated material into the filters. The elutriated material was generated only by attrition/fragmentation of in-bed sorbent inasmuch as fines were absent in the solid feed and, furthermore, comminution of sand was negligible.

The characterization of all the investigated materials was performed by X-Ray Diffraction (XRD) analysis. The sorbent material, derived from a full-scale FB reactor waste reactivated by water hydration, was also characterized by means of simultaneous Differential Thermal/Thermo Gravimetric Analysis (DTA/TGA). Moreover, TGA was employed for the determination of the concentration of ettringite, CaCO$_3$ and Ca(OH)$_2$: the quantitative evaluation of ettringite was made assuming that the related thermal effect is due to a concentrated weight loss of 24 water molecules per ettringite molecule [8].

**RESULTS AND DISCUSSION**

The chemical composition of FBC fly ash is shown in Table 1.

Tab. 1 FBC fly ash chemical composition, major oxides, Wt%.

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>SO$_3$</th>
<th>L.O.I.*</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.0</td>
<td>11.7</td>
<td>27.2</td>
<td>4.6</td>
<td>15.2</td>
<td>10.2</td>
<td>95.9</td>
</tr>
</tbody>
</table>

*Loss on ignition @975°C*
The main crystalline phases are, in the order, anhydrite, lime, quartz and hematite (Table 2). The high concentration of CaSO$_4$, CaO and Al$_2$O$_3$ makes this waste suitable for generating a significant ettringite amount upon hydration.

Tab. 2 FBC fly ash qualitative phase composition evaluated by XRD analysis: $A=$anhydrite (CaSO$_4$), $Q=$quartz (SiO$_2$), $L=$lime (CaO), $H=$hematite (Fe$_2$O$_3$), $E=$ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O), $C=$calcite (CaCO$_3$).

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>Q</th>
<th>L</th>
<th>H</th>
<th>E</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample as received</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sample after hydration</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Hydrated sample after calcination</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrated sample after sulphation</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Symbols indicate peak intensity: low = +; medium = ++; high = +++.

Table 2 and Figure 1 report the XRD analysis results and the DTA/TGA thermograms for the hydrated-reactivated FBC waste, respectively. Ettringite is by far dominant among the hydration products, its concentration in the reacting system being about 50% by mass. Calcium hydroxide, generated during the early stages of the hydration process, contributes to the formation of both ettringite [11] and calcium carbonate. As far as the reactants are concerned, unconverted quartz and hematite are still present together with anhydrite, not completely transformed into ettringite.

![Fig. 1 DTA/TGA thermograms of the industrial FBC fly ash hydrated for 48 h at 70°C.](image)

With regard to the calcination of the hydrated ash, it can be observed that the thermal decomposition of ettringite contained in the reactivated material has usefully given the lime exploitable for SO$_2$ uptake (Table 2). The other crystalline phases detected were anhydrite, quartz and hematite. The former derives from both the unhydrated CaSO$_4$ and the product of ettringite calcination; the latter two are associated with the phases initially present in the industrial fly ash, not involved in the hydration and calcination processes.
Finally, the XRD results on the sulphated sorbent, indicated in the lower part of Table 2, suggest that a quantitative transformation of the available lime into calcium sulphate has occurred.

Figure 2a shows the sulphur uptake efficiency $\eta(t)$ as a function of the sulphation time for the hydrated FBC ash whose available specific lime content is equal to 1.2 mmol per gram. It can be observed that at the beginning of the batch sulphation test $\eta$ reaches its maximum value (81%); subsequently it progressively declines during the test. The sulphation behaviour of the material investigated appears therefore highly satisfactory, even though it is worse than that shown by a synthetic ettringite (Figure 2a) previously investigated and operated under the same experimental conditions [8]. Synthetic ettringite was obtained as a highly porous flake-like precipitation product, having an available specific lime content of 2.4 mmol per gram. Such value, double than that of the hydrated FBC ash, accounts for the differences in sulphur uptake efficiency observed especially at the beginning of the test. Figure 2b reports the degree of calcium conversion $X_{Ca}(t)$ as a function of the sulphation time for both sorbents.

It is worth nothing that $X_{Ca}$ for the hydrated FBC ash approaches the value of 92%, much higher than that observed for commercial limestones commonly employed (30-40%, [12]). Moreover, throughout the test, $X_{Ca}$ for the hydrated FBC fly ash is higher than that measured for synthetic ettringite (Figure 2b). Hence, the ettringite contained in the hydrated FBC ash is even more reactive than the ettringite synthetically prepared.

Such difference in reactivity is illustrated in Figure 3 which reports the intrinsic sulphation kinetic constant $K$ as a function of the degree of calcium conversion [8]. $K$ is defined as

$$K(t) = \frac{\frac{dX_{Ca}}{dt}}{C_{SO_2}^{out}(t)} = \frac{F_{SO_2}^{in} - F_{SO_2}^{out}(t)}{n_{CaO} \cdot C_{SO_2}^{out}(t)}$$

where $C_{SO_2}^{out}(t)$ is the SO$_2$ concentration measured in the exhaust gas. For a limited $X_{Ca}$ range (0-21%) the $K$ values for synthetic ettringite are higher than those observed for the hydrated FBC ash. However, these latter are greater than the $K$ values for synthetic ettringite within a much wider $X_{Ca}$ range.
**Fig. 3** Intrinsic kinetic constant for hydrated FBC ash and synthetic ettringite sulphated in the FB reactor for 100 minutes at 850°C.

Table 3 reports the fines elutriation rate $E(t)$ obtained during the batch sulphation test of the hydrated FBC ash. $E$ changes with time according to a decreasing pattern resembling that typically observed for limestone [9]. This trend can be explained in the light of the following considerations:

i) sorbent dehydration in the early stage of the test determines particle fragmentation as a consequence of both thermal shock and water release: therefore particle rounding off and removal of surface asperities are significant, leading to high $E$ values;

ii) in the late stage of the test, attrition is dominated by strengthening of the particle surface layer as CaO reacts to form CaSO$_4$ in the outer shell, determining lower $E$ values.

**Tab. 3** Fines elutriation rate during batch sulphation of hydrated FBC ash operated in the FB reactor for 100 minutes at 850°C.

<table>
<thead>
<tr>
<th>process time interval, minutes</th>
<th>$E(t)$, g/minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5</td>
<td>0.0718</td>
</tr>
<tr>
<td>5-10</td>
<td>0.0370</td>
</tr>
<tr>
<td>10-15</td>
<td>0.0292</td>
</tr>
<tr>
<td>15-20</td>
<td>0.0378</td>
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<tr>
<td>20-30</td>
<td>0.0193</td>
</tr>
<tr>
<td>30-40</td>
<td>0.0244</td>
</tr>
<tr>
<td>40-50</td>
<td>0.0222</td>
</tr>
<tr>
<td>50-60</td>
<td>0.0189</td>
</tr>
<tr>
<td>60-70</td>
<td>0.0171</td>
</tr>
<tr>
<td>70-80</td>
<td>0.0252</td>
</tr>
<tr>
<td>80-90</td>
<td>0.0207</td>
</tr>
<tr>
<td>90-100</td>
<td>0.0197</td>
</tr>
</tbody>
</table>

$\int E(t)\,dt \approx 2.55 \text{ g}$

From Table 3 it can be observed that the total amount of elutriated fines ($\int E(t)\,dt$) is equal to 2.55 g (25.5% of the inlet sorbent mass), while for synthetic ettringite and limestone (both operated under the same experimental conditions, [8]) $\int E(t)\,dt$ is equal to 1.11 g and 0.58 g, respectively. From these data it can be argued that the attrition/fragmentation tendency
of the hydrated FBC ash investigated in this study is relatively high. This should be analyzed in the light of its twofold effect: while attrited fines are characterized by shorter residence times in the reactor, they exhibit an enhanced kinetics of sulphur uptake and could partly account for the higher $X_{Ca}$ values observed for the hydrated FBC ash.

CONCLUSIONS

The ettringite sulphur uptake ability is related to the lime made available by its thermal decomposition. An ettringite-rich industrial FBC reactivated ash, obtained by hydration at 70°C for 48 h, has proved to be a satisfactory SO$_2$ sorbent when submitted to a laboratory scale evaluation test. The desulphurizing behaviour of ettringite contained in the sorbent was better than that of a synthetically prepared ettringite previously investigated. At the end of the sulphation test, the degree of calcium conversion was 92% for the sorbent, 58% for the synthetic ettringite. However, the sulphur uptake efficiency for the latter was higher inasmuch as phases not useful for SO$_2$ uptake were also present in the sorbent. As far as the attrition/fragmentation propensity is concerned, the sorbent investigated has shown a relatively high fines elutriation rate, whose negative effect can be counterbalanced by the enhanced kinetics of the attrited material.

REFERENCES