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Reuse of landfilled FBC residues

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Two aspects of the possible reactivation of fluidized bed combustion (FBC) residues are considered. One is the behaviour of aluminosulfates such as ettringite, which may form when excess water is used in hydration methods designed to reactivate the lime in the FBC residues. The second is the behaviour of compounds such as calcium aluminates, silicates or ferrites ('other calcium compounds' or OCC) that are produced by reactions in the fluidized bed. In both cases, the possibility of recovering the CaO contained in these materials for retention of SO_2 when they are reintroduced into a combustor is assessed. It was found that ettringite is an excellent sulfur sorbent under FBC conditions, with reactivity superior to normal limestones. The CaO moiety in the OCC is not easily reactivated by hydration. Unhydrated, they do react in a sulfating atmosphere like that of the combustor, but their performance as sorbents is much poorer than limestone and varies with the nature of the compound. © *1997 Elsevier Science Ltd.*

(Keywords: FBC residues; calcium compounds; desulfurization capacity)

One of the major advantages of fluidized bed combustion (FBC) boilers, both circulating and bubbling, is the possibility of using limestone or dolomite to capture SO_2 in the combustor itself. In units operating at atmospheric pressure, limestone or dolomite first calcines and then the CaO component reacts with SO_2 by the global reactions:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 182.1\ \mathrm{kJ\ mol^{-1}} \qquad (1)$$

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \quad \Delta H = -481.4\ \mathrm{kJ\ mol^{-1}} \qquad (2)$$

The molar volumes of calcite (the most common form of $CaCO_3$ in limestone[1]), CaO and $CaSO_4$ (as anhydrite) are ~37, 17 and 46 $\mathrm{cm^3\ mol^{-1}}$ respectively[2]. This means that at atmospheric conditions, limestone calcines from a relatively non-porous material (with a natural porosity between 0.3 and 12%) to an extremely porous solid, with a porosity of > 50% [3]. However, the product of sulfation then tends to block the original pores and a sulfate layer is thus formed which tends to prevent further reaction between the unreacted CaO and SO_2; in larger particles, there is typically a well-distinguished inner core of CaO, surrounded by an outer sulfated layer. Thus, whereas conventional wet flue gas desulfurization (FGD) systems using lime or limestone can achieve nearly stoichiometric calcium utilization, FBC systems are associated with much lower Ca utilization levels and even 45% utilization of the Ca in the sorbent is considered excellent performance[4]. In consequence, the issue of improving sulfur capture in FBC is of key importance to the development of the technology for use with high-sulfur fuels.

REACTIVATION PROCESSES

Hydrates

Most of the concepts developed to reactivate spent limestone from atmospheric FBC involve hydrating the free lime content of the FBC residues to produce $Ca(OH)_2$, since this has been shown to be able to reactivate the sorbent for reuse in the combustor, the resulfation potential increasing almost linearly with the degree of hydration of the available free lime content[5,6]. Ideally, any hydration process ought to deliver a dry product. Such products are more easily handled and can also be pneumatically conveyed. In addition, dry products do not carry the economic penalty involved in vaporizing excess water in an FBC boiler.

There is at least one industrial process, the CERCHAR process, which can totally hydrate the free lime in such residues and still deliver a dry product, and this has been shown to have excellent potential for reactivation[7,8]. However, under many circumstances these hydrated residues are likely to be produced in a wet state, and if they are stored or conveyed in the form of wet pastes or slurries, the $CaSO_4$ component of the ash begins to react with any Al in the fuel-derived ash, to form aluminosulfates such as ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ or $Ca_6[Al(OH)_6]2(SO_4)_3{\cdot}26H_2O$, the 26 molecules of H_2O being the water of hydration, which is liberated from ettringite at temperatures between 50 and 100°C)*. Similarly, landfilled materials in the presence of ambient moisture will react to form compounds such as ettringite[9,10]. This then opens the question as to the likely performance of such materials as sulfur sorbents, if reground and re-injected into the combustor.

Other calcium compounds

There is one other possible route for the loss of free lime content in the solid residues, and that is the formation of other calcium compounds (OCC), such as aluminates, ferrites and silicates, presumably primarily by reaction of the fuel-derived ash with the calcined limestone by

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* It is important to note in this context that the formation of ettringite is a cementitious process which leads to the formation of hardened material.

solid-state reactions. The potential for reactivation of this combined lime should also be considered.

The existence of these compounds is usually ignored, although it has been recognized when processes such as agglomeration occur, in which case their formation has been ascribed to the existence of 'hot spots' and interactions between the impurities in limestone or to reactions between CaO and other minerals inherent in the ash itself[11,12]. Their formation has also been noted in the high-calcium ashes obtained from fuels such as lignitic coals and oil shale[13].

Unfortunately, it is often assumed that the free lime content of solid FBC residues can be calculated on the basis of the elemental analysis, taking only into account the degree of formation of sulfates, carbonates and possibly sulfides. In some cases this assumption does not lead to serious error, but frequently it leads to a significant overestimate of the free lime content of the residue, and it has been shown that in some cases up to 40% of the nominal free lime content was in fact present as OCC[14,15]. Similarly, recent analysis of bed ash from the Point Aconi 165 MW_e CFBC plant in Nova Scotia (which is currently the largest operating CFBC boiler in the world) determined that the free lime content of the ashes was 14.9 wt%, while OCC expressed in terms of CaO equivalent were 6.6 wt%, which leads to a 31% overestimate for the free lime content by traditional calculations. Such very high levels of conversion of CaO to OCC also support the contention that these compounds are formed by interactions between the fuel ash and limestone and are not simply due to impurities in the limestone itself.

So far as is known, there have been no studies of the sulfation behaviour of OCC. As to the possibility of hydrolysis reactions producing $Ca(OH)_2$, it should be noted that the usual OCC found in FBC ashes are gehlenite, calcium ferrite or aluminoferrite and larnite. Of these compounds, gehlenite is virtually inert and the others, particularly ferrite, are attacked only very slowly by water. In this case, the potential for reactivation of these materials by hydration will not be significant. Current data for instance show that gehlenite, larnite and dicalcium ferrite fail to hydrate after exposure to excess water for 5 days at 75°C, which would be sufficient to hydrate the CaO in typical highly calcic FBC residues in a matter of hours.

EXPERIMENTAL

Ettringite

Earlier work showed that spent bed residues which were hydrated with 30 wt% excess water contained ~9 wt% ettringite. When sulfated in a thermogravimetric analyser (t.g.a.), the sample showed a high degree of conversion—~99%—of the total CaO available, which corresponds to complete conversion of the CaO in ettringite[9]. However, it is possible to argue that there was something anomalous about these results, given the unusually high degree of sulfation of this sample. To examine whether such materials do indeed decompose releasing their CaO content and making it quantitatively available for sulfation, it was decided to synthesize ettringite and study its decomposition behaviour.

Ettringite was synthesized following the procedure of Mylius, as indicated by Taylor[10]. After filtration, the precipitate was washed with acetone to remove water, then washed with ether and dried at room temperature. The product obtained was analysed using X-ray diffraction (XRD), which was performed on a Siemens D 500 instrument with filtered Cu radiation and a Kevex detector. Thermogravimetry was performed in an O_2-free argon stream, and differential scanning calorimetry (d.s.c.) was also carried out.

OCC

To obtain some information about the 'other calcium compounds', the sulfation behaviour of several compounds (obtained from Construction Technologies Laboratories, Skokie, IL) was studied. The compounds were:

gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$)

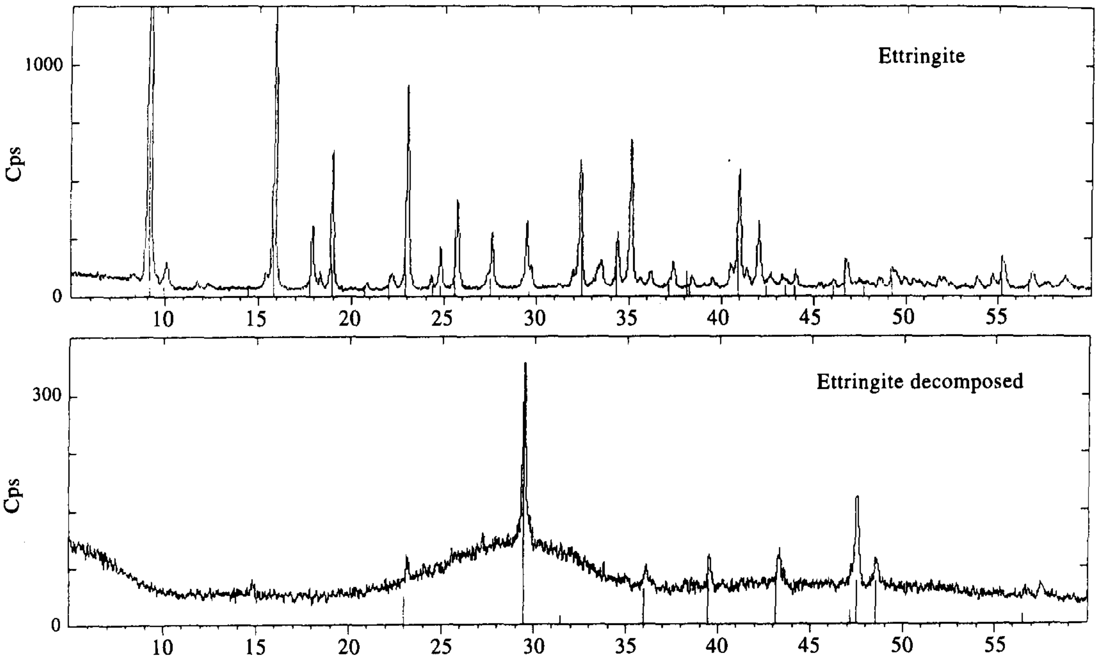

Figure 1 X-ray diffractograms: upper, synthesized ettringite; lower, synthesized ettringite, after decomposition; 2θ scale

larnite ($2CaO{\cdot}SiO_2$)
dicalcium ferrite ($2CaO{\cdot}Fe_2O_3$)
tetracalcium aluminoferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$).

The first three have been found in FBC solids. Some substitution of Al for the Fe atoms has also been observed in the ferrite, although less than that corresponding to the last compound.

Two other materials were also studied for comparison. One was a limestone used for the 165 MW_e Point Aconi CFBC; it had a particle size in the range of 0.125–0.25 mm. The other was the synthesized ettringite.

These compounds were sulfated in a t.g.a. The sulfation was conducted at 850°C with synthetic flue gas containing 5000 ppmv SO_2, 2.5 vol.% O_2, 15 vol.% CO_2 and the balance N_2.

RESULTS AND DISCUSSION

Ettringite synthesis

The X-ray diffraction pattern of the ettringite prepared is given in the upper section of *Figure 1*. All the main peaks correspond to ettringite; some of the minor peaks indicate calcite ($CaCO_3$) as impurity. The t.g.a. recording (*Figure 2*) shows a main water loss centred at 130°C and a minor loss centred around 270°C; a small loss at ~720°C corresponds to decomposition of calcite. This confirms the composition observed by XRD and permits the amount of $CaCO_3$ to be estimated as ~5 wt%. The d.s.c. trace (*Figure 3*) shows a strong endotherm at ~158°C, again typical of ettringite, and a smaller diffuse endotherm centred around 250°C. Observation with scanning electron microscope showed the typical clusters of needles, a few tenths of a micrometre thick and ~10 μm long. Taken as a whole, these observations reveal a sample of ettringite with only 5 wt% of calcite as impurity. This was considered satisfactory for the intended test.

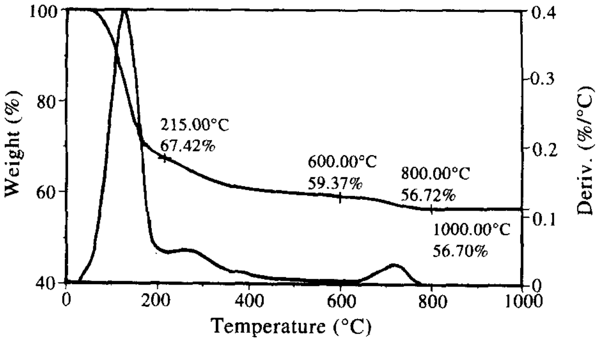

Figure 2 Thermogravimetric analysis of synthesized ettringite

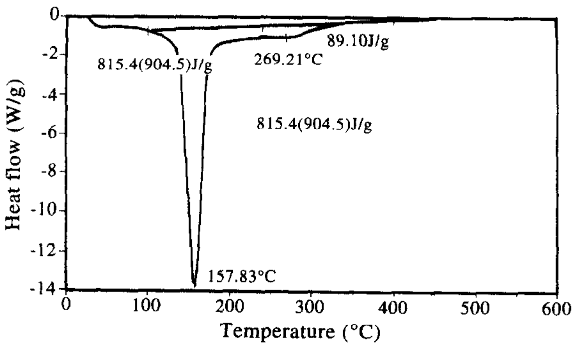

Figure 3 Differential scanning calorimetric analysis of synthesized ettringite

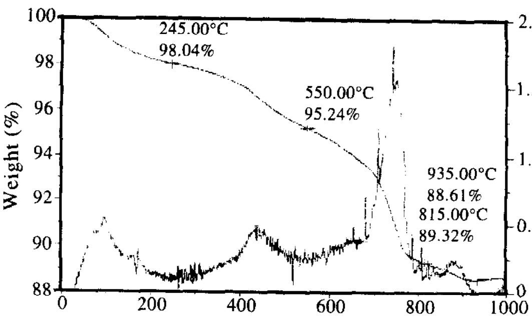

Figure 4 Thermogravimetric analysis of synthesized ettringite, after decomposition

A portion of the synthesized ettringite was heated at 200°C for 1 h. The residue was analysed by XRD and t.g.a. The X-ray diffractogram (lower part of *Figure 1*) indicates that the ettringite has totally disappeared. The pattern shows well-defined peaks of $CaCO_3$ and two humps (around 5 and 30°) which probably correspond to amorphous hydrated Al oxide. Two peaks barely distinguishable from the background noise ($d = 5.99$ and 2.35 Å, or $2\theta = 14.8°$ and 38.3°) are typical of crystalline boehmite, γ-AlO_2H. The main peak of $CaSO_4$ at $2\theta = 25.4°$ is not detectable above the background noise, although the compound must have been present. The t.g.a. trace of the decomposed ettringite (*Figure 4*) shows a weight loss around 420°C, which may be attributed to water loss from the hydrated Al oxide, and a large loss at 740°C, corresponding to $CaCO_3$ decomposition.

As a check, a titration was performed on the decomposed product, with 0.02M HCl and phenolphthalein. The titration, which should include all the CaO, free (corresponding in total to half of the Ca in the decomposed ettringite molecule) or carbonated, was continued until the pink colour did not return on boiling the solution. The result coincided within 2% with the expected value, thus confirming that all the CaO in the ettringite molecule becomes available in the decomposition.

Sulfation

The test results are represented by a *reactivity index* (RI) and a *sulfur absorption capacity* (CI). RI is defined as the number of moles of sorbent in the limestone or the compound per mole of sulfur captured, and CI as the number of grams of sulfur captured per kilogram of limestone or sorbent compound. In determining both indices, it was assumed that both CaO and any MgO in the sorbent are capable of fully sulfating. In practice, the MgO component of any limestone or dolomite does not sulfate to any appreciable extent in an FBC system, but this definition allows the effectiveness of both limestone and dolomitic stones to be compared on a mass basis. All the calculations of the indices are based on a sulfation period of 1 h. The results are summarized in *Table 1*.

It can be seen that all the OCC are able to sulfate. However, their ability to sulfate is generally poor. This is particularly so for the very inert gehlenite.

Ettringite is seen to be considerably more reactive than the limestone. When this sample was further sulfated for a total of 24 h, it showed an overall conversion of 95.3%. For

Table 1 Sulfation results

Compound	RI (mol mol^{-1})	CI (g kg^{-1})
Limestone	3.27	92.6
Ettringite	1.21	77.8
Gehlenite	74.0	3.16
Larnite	23.9	15.6
Dicalcium ferrite	6.34	32.7
Tetracalcium aluminoferrite	11.3	23.3

comparison, FBC residues from the Point Aconi CFBC (using nominally the same limestone for which data are presented in *Table 1*) took 60 days to increase its sulfation from 50 to 72% when held in an oven at 850°C in a gas stream with the composition 10000 ppmv SO_2, 3 vol.% O_2 and the balance N_2. Similar conclusions have been reached by other workers for ettringite's ability to sulfate in the low-temperature regime ($< 400°C$), typical of 'cool-side' SO_2 capture processes[16].

CONCLUSIONS

Ettringite becomes totally decomposed at relatively low temperatures, losing water and giving a mixture of the three solid components. Of these, CaO can easily become carbonated, but this is immaterial for reuse in FBC, where $CaCO_3$ decomposes again. From the point of view of reactivation, all the CaO component, which corresponds to half the Ca contained in the molecule, must become available for further reaction and in particular for sulfation. The t.g.a. sulfation results in this study suggest that ettringite is much more reactive than a typical limestone. This means that production of aluminosulfates, either when the ash is wet (or more precisely has water available in its pore structure) or if taken from a landfill, poses no chemical limitation to the reuse of such residues as sulfur sorbents.

For the OCC, the situation is less clear. They are too slow to react with water for hydration to be considered as an effective reactivation step for these materials. None the less, all these compounds have the potential to be sulfated, albeit at much slower rates than limestones. There is still a question of how much the low rates of sulfation depend on the morphology of the standards used, and whether their behaviour differs from that of the same materials in FBC residues. Further study is warranted to clarify this point.

ACKNOWLEDGEMENTS

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