



## Study of the hydrothermal treatments of residues from fluidized bed combustors for the manufacture of ettringite-based building elements



Antonio Telesca<sup>a</sup>, Daniela Calabrese<sup>a</sup>, Milena Marroccoli<sup>a</sup>, Gian Lorenzo Valenti<sup>a</sup>, Fabio Montagnaro<sup>b,\*</sup>

<sup>a</sup> Scuola di Ingegneria, Università degli Studi della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

<sup>b</sup> Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, 80126 Napoli, Italy

### ARTICLE INFO

#### Article history:

Received 5 March 2014

Received in revised form 22 April 2014

Accepted 5 May 2014

Available online 22 May 2014

#### Keywords:

By-product utilization

Fluidized bed combustion waste

Building industry

Prefabrication

Hydrothermal treatment

Ettringite

### ABSTRACT

Fluidized bed combustion (FBC) waste is generally unsuitable for making ordinary cements and concretes, and its alternative uses are therefore worthy of consideration. In the present work, FBC waste is investigated as a potentially suitable single raw material for the manufacture of building components based on ettringite, a compound characterized by low density, high fire resistance, significant mechanical strength and usefulness as the main component of preformed lightweight building materials. The hydration behaviour of two FBC waste samples (a fly and a bottom ash) was explored within curing periods comprised between 2 and 24 h at 55 °C, 70 °C and 85 °C. X-ray diffraction and differential thermal analysis were employed as main experimental techniques in order to evaluate the distribution of the hydration products. The role of the raw ash chemical and mineralogical composition, operating temperature and time in the ettringite formation was highlighted. The fly ash was more prone to generate ettringite which, after 2 h-curing time, tended to form and decompose earlier, as the curing temperature and time were further increased. The selectivity of the reactants toward ettringite can be enhanced by the addition of blending components.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Ettringite ( $6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$ ) is a calcium sulphoaluminate hydrate produced by the reactions of gypsum or anhydrite with calcium aluminates and water during the early hydration of Portland cement. It is well known that ettringite, in spite of the limited quantity generated, can regulate both setting and initial hardening of Portland cement [1]. Ettringite is water insoluble and has very interesting binding properties, due to the considerable surface energy and the large surface area of its particles [2].

Ettringite also represents the main hydration product of calcium sulphoaluminate-based cements which are special hydraulic binders able to behave as shrinkage-compensating and self-stressing [3–5] or rapid-hardening and dimensionally stable [6–11] cements. Moreover, ettringite can be a very useful component of preformed lightweight building elements, owing to its low density, high fire-resistance and significant mechanical strength. These ettringite-based materials can be obtained by hydration treatments of mixtures containing calcium sulphate and oxides or hydroxides of calcium and aluminium: curing temperatures higher than room temperature are generally required to give an appreciable ettringite formation rate [12–19].

As far as the burning of solid fuels is concerned, the fluidized bed combustion (FBC) technology is very effective and also ensures a low

environmental impact [20–25]. However, a considerable drawback of this technology is represented by both (i) great quantity and (ii) poor quality of the related solid residues (composed by coal ash and exhausted calcium-based sulphur sorbent), in comparison with the ashes coming from traditional pulverized coal combustion plants. The former is due to the need of an overstoichiometric sorbent feed, because of the incomplete sorbent sulphation; the latter is associated with the peculiar chemical and mineralogical characteristics of FBC waste, i.e. its high concentration of free calcium oxide and low amount of amorphous phase (owing to the relatively low combustion temperature). CaO can interact in landfill with atmospheric agents, giving rise to expansive phenomena, loss of stability and subsoil alteration [26, 27], while the reduced glass content of coal ash lowers its pozzolanic activity and compromises its reuse in traditional fields of utilization such as ordinary cements and concretes [28,29].

To find alternative uses for FBC waste is therefore of critical importance. Its major constituents are oxides entering into the ettringite composition. While in the past the formation of ettringite upon hydration of FBC ash was successfully investigated with the aim of obtaining highly-active  $\text{SO}_2$  sorbents [30–34], in the present work FBC waste is seen as a potentially suitable single raw material for the manufacture of building components based on ettringite. These materials can replace the traditional mortar or concrete products in which the main binding phase is calcium silicate hydrate generated by Portland cement or blast-furnace slag hydration as well as pozzolanic reaction.

\* Corresponding author. Tel.: +39 081 674029; fax: +39 081 674090.  
E-mail address: [fabio.montagnaro@unina.it](mailto:fabio.montagnaro@unina.it) (F. Montagnaro).

The hydration behaviour of two FBC waste samples (a fly and a bottom ash) is here investigated under various operating conditions, using X-ray diffraction (XRD) and differential thermal analysis (DTA) as main experimental techniques.

## 2. Materials and methods

As raw materials for this investigation, two samples of FBC fly and bottom ash (labeled *F* and *B*, respectively), generated in a full-scale 790 MW<sub>th</sub> circulating reactor (fired with a 80%–20% by mass binary mixture consisting of South African and Italian coal, respectively), were used. The samples, supplied by the ENEL Research Centre of Turturano (Brindisi, Italy), were ground in a laboratory mill to pass the 90 μm-sieve before the characterization tests.

*F* and *B* were paste hydrated with a 1.0 water/solid mass ratio and cured in a thermostatic bath at 55 °C, 70 °C and 85 °C from 2 h to 24 h. At the end of each established aging period (2 h, 8 h and 24 h), the hardened pastes were pulverized after grinding under acetone in an agate mortar (to stop hydration) followed by treating with diethyl ether (to remove water) and storing over silica gel–soda lime (to ensure protection against H<sub>2</sub>O and CO<sub>2</sub>).

As analytical techniques, X-ray fluorescence (XRF) and XRD analyses were employed for the evaluation of FBC waste chemical and mineralogical composition using a BRUKER Explorer S4 instrument and a BRUKER D2 Phaser diffractometer (Cu Kα radiation, 0.05°/s scanning rate), respectively. XRD analysis was also utilized for the characterization of the hydrated samples, together with DTA carried out through a NETZSCH Tasc 414/3 apparatus (20–700 °C temperature range, 10 °C/min heating rate).

## 3. Results and discussion

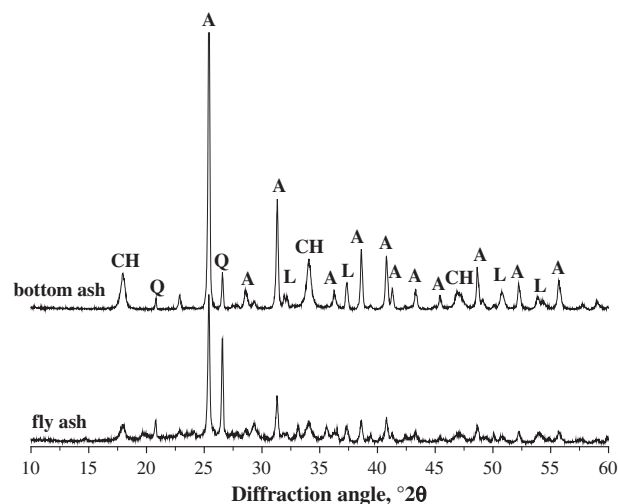
The chemical composition of *F* and *B* is shown in Table 1. Taking into account that SO<sub>3</sub> is in practice fully involved in the CaSO<sub>4</sub> formation, the reported data imply that the CaSO<sub>4</sub> and free CaO contents were, respectively, 21.8% and 15.2% for *F*, and 51.8% and 22.6% for *B*. While the bottom ash was very rich in the sorbent-derived (sulphocalcic) fraction, the elutriated fly ash was higher in silica, alumina, iron oxide and unburnt carbon (loss on ignition), due to its greater coal ash concentration connected with peculiar FBC operating conditions. The values here reported are typical for fly and bottom ash generated in FBC plants [32,34].

Fig. 1 shows the XRD patterns for *F* and *B*: (i) anhydrite, quartz, portlandite and lime for the former, and (ii) anhydrite, portlandite, lime and quartz for the latter, in the decreasing order, were detected as main crystalline phases. Calcium hydroxide arose from CaO hydration by weathering of both FBC ashes, before their sampling. XRD data confirm the major role played by the sulphocalcic fraction in the bottom ash and that of silica in the fly ash whose Al- and Fe-containing phases did not display appreciable peak intensities, most likely because of their amorphous nature [31].

**Table 1**  
Chemical composition of FBC fly (*F*) and bottom (*B*) ashes, mass %.

	<i>F</i>	<i>B</i>
CaO	24.2	43.9
SO <sub>3</sub>	12.8	30.5
Al <sub>2</sub> O <sub>3</sub>	13.7	3.8
SiO <sub>2</sub>	23.2	13.0
MgO	1.0	0.7
P <sub>2</sub> O <sub>5</sub>	–	0.1
TiO <sub>2</sub>	0.8	0.3
Fe <sub>2</sub> O <sub>3</sub>	6.7	1.8
Mn <sub>2</sub> O <sub>4</sub>	0.1	–
l.o.i. <sup>a</sup>	16.3	4.9
Total	98.8	99.0

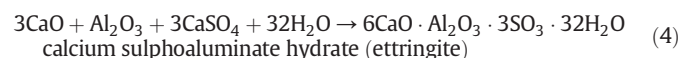
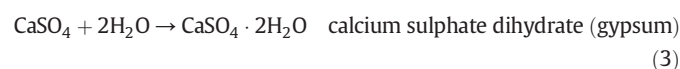
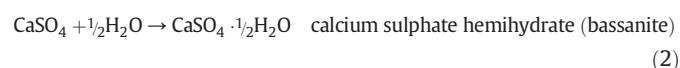
<sup>a</sup> Loss on ignition at 950 °C, according to EN 196-2 Standard for cements.



**Fig. 1.** XRD patterns for FBC bottom (up) and fly (down) ash: A = anhydrite (CaSO<sub>4</sub>), CH = portlandite (Ca(OH)<sub>2</sub>), L = lime (CaO), and Q = quartz (SiO<sub>2</sub>).

Table 2 indicates the water/solid, alumina/lime and calcium sulphate/lime mass ratios related to the composition of the hydrating samples, together with the corresponding stoichiometric values required by the ettringite (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O) formation. It can be argued that: (i) a water excess was employed for the hydration of both samples; (ii) the limiting reactants for the ettringite formation were calcium sulphate and alumina for *F* and *B*, respectively. Being the defect of alumina (–66.7%) for *B* larger than that (–41.7%) of calcium sulphate for *F*, this latter ash had a more suitable composition for the ettringite formation upon hydration. However, for both samples a higher concentration of ettringite and a reduced amount of unsuitable soluble phases (portlandite and gypsum) could be advantageously obtained by blending *F* and *B* with additional sources of calcium sulphate and alumina, respectively.

The hydration process under investigation is generally characterized by the following main reactions:



The sources of lime and calcium sulphate necessary for the ettringite formation, according to the reaction (4), can be also given by the hydration products of the reactions (1), (2), (3). Differently from other constituents of FBC ashes, crystalline silica is not expected to have a role

**Table 2**  
Water/solid, alumina/lime and calcium sulphate/lime mass ratios for *F* and *B*, and related stoichiometric values required by the ettringite formation.

	Water/solid	Alumina/lime	Calcium sulphate/lime
<i>F</i>	1.0	0.9	1.4
<i>B</i>	1.0	0.2	2.3
Stoichiometric values	0.8	0.6	2.4

Download English Version:

<https://daneshyari.com/en/article/209715>

Download Persian Version:

<https://daneshyari.com/article/209715>

[Daneshyari.com](https://daneshyari.com)