

# Use of Fluidized Bed Combustion Residues and Alumina Powder as Components of Ettringite-Based Aerated Building Elements

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The use of industrial wastes and by-products for making construction materials unequivocally gives a pronounced environment-friendly character to their manufacturing process. Two binary (M1, M2) and one ternary (M3) mixtures, based on alumina powder, fluidized bed coal combustion fly- and/or bottom-ash were submitted to hydrothermal treatments in order to generate aerated building elements based on ettringite ( $6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$ ); ettringite is a compound characterized by low density, water insolubility, high fire resistance and significant mechanical strength. The M1 – M3 systems were hydrated in a thermostatic bath (100 % R.H) at 55 °C and 70 °C for aging periods ranging from 2 h to 28 d; the hydrated samples were submitted to both differential thermal–thermogravimetric and X-ray diffraction analyses for assessing the formation of the hydration products. In this regard, the ettringite generation, being also dependent on the operating temperatures and times, was observed within all the investigated systems. Furthermore, the best results in terms of both ettringite concentration and formation rate were exhibited by the M2 system at 70 °C after 2 d of curing.

## 1. Introduction

At the present time, there is undoubtedly an increasing interest towards the use of wastes coming from industrial activities for the production of Portland clinkers (Mikulcic et al., 2013), ordinary (Bernardo et al., 2007) and special (Pace et al., 2011) cements, common (Correia et al., 2011) and lightweight (Pelisser et al., 2012) concrete, paving blocks (Wattanasiriwech et al., 2009), road pavements (Ondova et al., 2011), prefabricated building materials (Telesca et al., 2013) and innovative adsorbent materials for heavy metals removal (Andini et al., 2013) mainly in water treatment (Balsamo et al., 2013). In particular, the utilization of *fluidized bed combustion* (FBC) residues, which generally have a low potential for the reuse in the traditional fields of employment [e.g., ordinary cements and concrete (Montagnaro et al., 2005)], due to both the poor pozzolanic behaviour and the exothermal/expansive phenomena occurring during their hydration (which also complicate the landfill disposal), is worthy of consideration (Marroccoli et al., 2009). The FBC wastes are mainly composed by combustion ash as well as calcium sulfate and unconverted lime (deriving from the in-situ  $\text{SO}_2$  removal by means of limestone-based sorbents). Viable alternatives to potential uses of FBC residues have been widely experienced in the past. They were investigated (i) with the purpose of obtaining alternative  $\text{SO}_2$  sorbents (Montagnaro et al., 2008) by means of water (Bernardo et al., 2004)/steam (Montagnaro et al., 2009) hydration–re-activation processes, (ii) for the synthesis of *calcium sulfoaluminate* (CSA) cements (Marroccoli et al., 2010c), namely special hydraulic binders obtained from non-Portland clinkers, and (iii) in the manufacture of ettringite-based building materials (Telesca et al., 2014a). Ettringite, namely a hexacalcium trisulfoaluminate hydrate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ), is a compound characterized by good binding properties (Bianchi et al., 2009), high water- and fire-resistance (Manzano et al., 2012), as well as satisfactory

mechanical strength (Hargis et al., 2014). It represents the early hydration product in ordinary Portland cements (from the reactions of gypsum or anhydrite with calcium aluminates and water), and the main hydration product of CSA cements, binders characterized by high early mechanical strength (Marroccoli et al., 2007), low porosity (Valenti et al., 2012), drying-shrinkage (Telesca et al., 2014b) as well as considerable impermeability and chemical resistance (Bernardo et al., 2006). The CSA cements are very interesting hydraulic binders inasmuch as they can couple the engineering properties useful for structural applications with environmentally friendly characteristics of their manufacturing cycle (Marroccoli et al., 2010a), such as low synthesis temperature and limestone requirement as well as reduced thermal input to the kiln and CO<sub>2</sub> generation (Marroccoli et al., 2010b).

This work was aimed at investigating the use of FBC wastes for the production, by means of hydrothermal treatments, of *aerated building materials* (ABM) based on ettringite. ABM are generally made from quartz-rich sand, lime, cement and calcium sulfate, with traces of aluminium powder as pore-forming agent (Narayanan and Ramamurthy, 2000). Their engineering properties are chiefly regulated by the binding products, mostly calcium silicate hydrate, which are made by hydrothermal reactions. A cellular green body, due to the generation of hydrogen gas bubbles produced by the reaction of aluminium with hydroxide of calcium or alkali, is also formed (Kurama et al., 2009). The novelty of the present research activity also lies in the utilization of alumina powder, namely an industrial by-product derived from the secondary aluminium manufacture, as pore-forming agent in substitution of the traditional powder of aluminium. The hydration behaviour of two binary and one ternary mixtures, cured under various operating conditions, was explored using *X-ray diffraction* (XRD) and *differential thermal–thermogravimetric* (DTA–TG) analyses.

## 2. Experimental

### 2.1 Materials

Two FBC wastes (bottom- and fly-ash, respectively labeled BFBC and FFBC) and alumina powder (AP) were employed as raw materials for the present experimental activity. The former were generated in a full-scale 790 MW<sub>th</sub> circulating FBC reactor, fired with an Italian fossil coal and supplied by the ENEL Research Centre of Turturano (Brindisi, Italy). The latter came from a secondary aluminium factory located in Northern Italy. The chemical composition of the investigated residues, determined by means of a *X-ray fluorescence* (XRF) apparatus, is reported in Table 1.

Table 1: Chemical composition of BFBC, FFBC and AP, mass %.

	BFBC	FFBC	AP
CaO	47.8	39.6	2.0
SO <sub>3</sub>	31.2	18.2	0.2
Al <sub>2</sub> O <sub>3</sub>	3.3	6.9	40.2
SiO <sub>2</sub>	12.0	16.0	39.4
MgO	0.8	1.8	6.6
P <sub>2</sub> O <sub>5</sub>	–	0.1	–
TiO <sub>2</sub>	0.2	0.3	–
Fe <sub>2</sub> O <sub>3</sub>	1.9	9.2	5.6
l.o.i.*	1.8	5.7	5.6
Total	99.0	97.8	99.6

\*loss on ignition at 950 °C, according to EN 196-2 Standard for cements.

Considering that all the SO<sub>3</sub> is completely involved in the formation of CaSO<sub>4</sub>, the reported data imply that calcium sulfate is equal to 53.0 % and 30.9 % for BFBC and FFBC. Moreover, compared to BFBC, FFBC was higher in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The larger sulfo–calcic fraction observed in the bottom ash is due to the larger exhausted sorbent concentration in this stream. This leaves behind, in the fly ash, a more relevant concentration of coal-derived material, able to justify the fly ash higher silico–aluminous fraction. Alumina and silica were also the main oxides detected in AP.

All the samples were also characterized by means of XRD analysis. The related XRD patterns are shown in Figure 1.

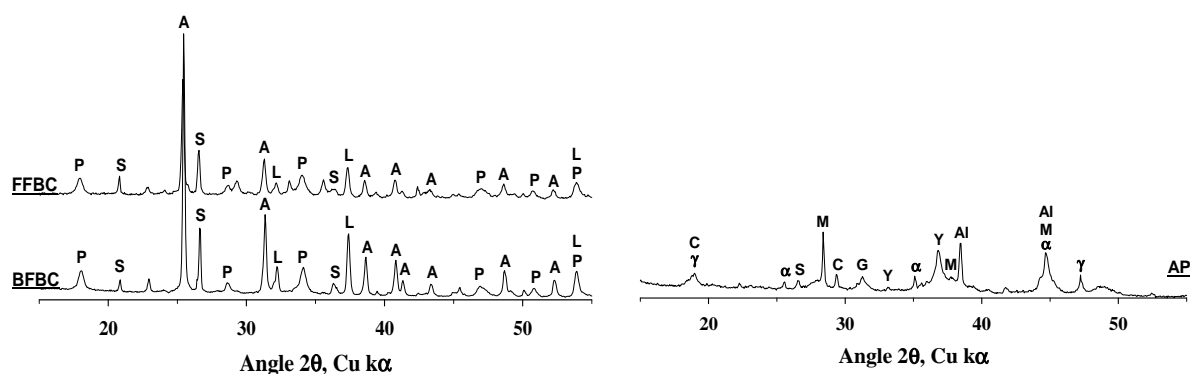


Figure 1: XRD patterns for BFBC-FFBC (left) and AP (right). P=portlandite ( $\text{Ca}(\text{OH})_2$ ), S=silica, L=lime; M=magnesium oxide, A=anhydrite, Y=mayenite ( $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ ), G=gehlenite ( $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$ ), C=calcium and aluminum oxide,  $\alpha$ = $\alpha$ -aluminium oxide,  $\gamma$ = $\gamma$ -aluminium oxide, Al=aluminium.

The main detected crystalline phases were anhydrite and silicon oxide for BFBC and FFBC, and  $\alpha$ -,  $\gamma$ -aluminium oxides, metallic aluminium and magnesium oxide for AP.

## 2.2 Proportioning of raw mixtures

Three mixtures (M1, M2 and M3) were investigated; their composition is illustrated in Table 2. M1 and M2 were binary mixtures respectively based on AP and BFBC or FFBC. M3 included, together with AP, both BFBC and FFBC, in a 40:60 mass ratio (the usual generation proportions of the two streams leaving the FBC reactor).

Table 2: Composition of mixtures M1–M3, mass %.

	M1	M2	M3
BFBC	80.0	–	36.0
FFBC	–	89.0	54.0
AP	20.0	11.0	10.0

The proportioning of M1 – M3 mixtures was made in order to maximize the ettringite concentration in the hydrated samples. In this regard, the potential concentration values of  $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$  was 81.9 %, 81.3 % and 73.0 % for M1, M2 and M3.

## 2.3 Hydration procedures

In order to maximize the formation of the hydration products, M1 – M3 systems were paste hydrated with a 1.0 water/solid mass ratio; they were cured in a thermostatic bath at 55 °C and 70 °C, 100 % R.H. (Cioffi et al., 1992) for curing periods ranging from 2 h to 28 d. The hardened pastes, at the end of each aging time, were, in the order, (i) pulverized after grinding under acetone (to stop hydration), (ii) treated with diethyl ether (to remove water) and (iii) stored in a desiccator containing silica gel and soda lime in order to ensure protection against  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (Telesca et al., 2014c).

## 2.4 Characterization techniques

A BRUKER Explorer S4 instrument and a BRUKER D2 Phaser diffractometer ( $\text{Cu } \kappa\alpha$  radiation, 0.05 °2 $\theta$ /s scanning rate) were respectively employed for XRF and XRD analyses. A NETZSCH Tasc 414/3 apparatus (20 ° – 1,000 °C temperature range, 10 °C/min heating rate) was utilized for DTA–TG analysis on the hydrated systems, which were also submitted to XRD evaluation. Phases such as ettringite, gypsum and calcium hydroxide were respectively identified (Taylor, 1997) through the following endothermic peaks: 145 °  $\pm$ 30 °C, 154 °  $\pm$ 9 °C and 480 °  $\pm$ 3 °C. TG analysis was also used for quantitative purposes, in order to determine the ettringite concentration in the hydrated samples. To this end, it was assumed that 24 water moles are lost by heating 1 mole of ettringite in the narrow temperature range corresponding to its strong endothermic effect.

### 3. Results and discussion

Figure 2 shows the TG results, in terms of ettringite concentration vs. curing time for M1, M2 and M3 mixtures hydrated at 55 °C and 70 °C. Up to 2 days of curing, the following sequence was observed in terms of both ettringite formation rate and concentration: M2(70 °C)>M2(55 °C)>M1(70 °C)>M3(70 °C)>M1(55 °C)>M3(55 °C). Namely, for short curing periods, it was obtained that the system M2, relying on the FBC fly ash, was more reactive toward ettringite than the system M1, relying on the FBC bottom ash. Furthermore, a positive effect of the curing temperature was recorded.

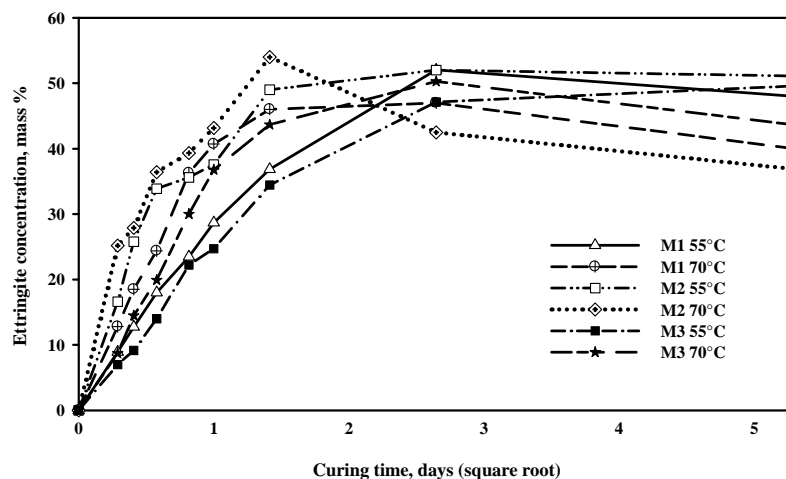


Figure 2: Ettringite concentration in the mixtures M1, M2 and M3 hydrated at 55 °C and 70 °C vs. curing time.

At longer curing periods, the ettringite concentration, for the systems M1 (70 °C) – M2 (70 °C) and M1 (55 °C) – M3 (55 °C), deeply decreases and increases, respectively. As far as the systems M2 (55 °C) and M3 (70 °C) are concerned, the ettringite concentration slightly increases up to 28 d of hydration. The negative effect of increasing the hydration temperature, generally observed for longer curing times, should be related to the higher ettringite decomposition rate, promoted under these operating conditions. Altogether, the best results in terms of ettringite formation were obtained for the mixture M2 hydrated at 70 °C for two days.

Figure 3 displays, as an example, the DTA results for the mixture M2 (the most reactive) hydrated at 55 °C and 70 °C. Up to 8 h of curing, the endothermic peaks related to gypsum and calcium hydroxide (respectively deriving from the hydration of calcium sulfate and calcium oxide) were present at both 55 °C and 70 °C. As far as the ettringite evolution is concerned, DTA data are in agreement with the TG results obtained and reported in Figure 2.

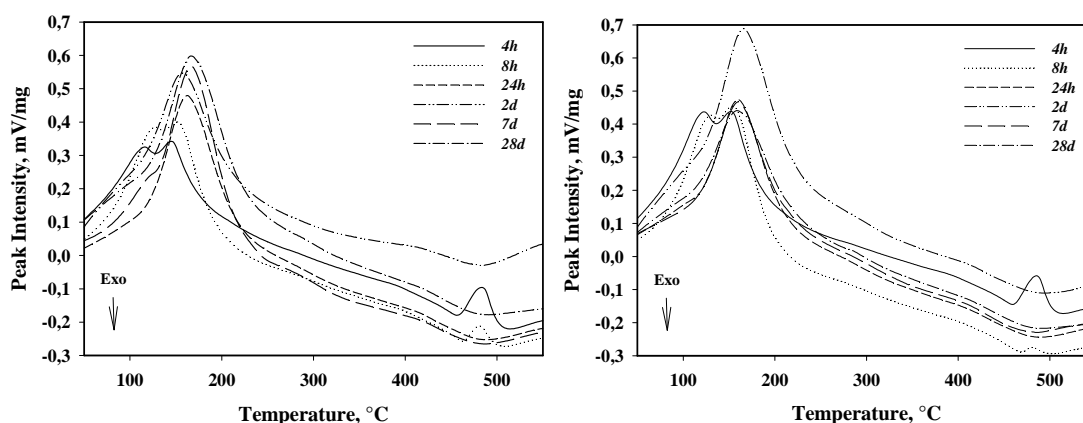


Figure 3: DTA results for M2 hydrated at 55 °C (left) and 70 °C (right) at various curing times.

The XRD data on the hydrated systems substantially agree with DTA results. As an example, Figure 4 shows the XRD patterns for the mixture M2 cured at 55 °C and 70 °C for 2 d.

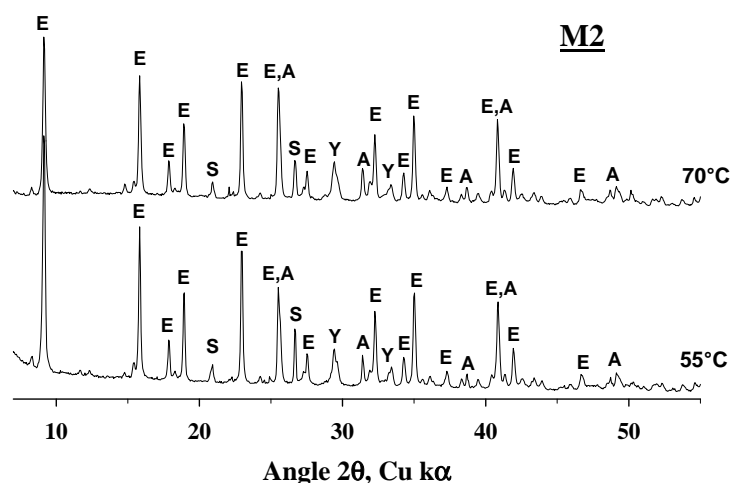


Figure 4: XRD patterns for the mixture M2 cured at 55 °C (down) and 70 °C (up) for 2 d. E=ettringite, A=anhydrite, Y=mayenite, S=silicon oxide.

Ettringite, together with unreacted phases (e.g. anhydrite, mayenite and silicon oxide), was present at both 55 °C and 70 °C.

#### 4. Conclusions

Mixtures containing fluidized bed combustion (FBC) residues and alumina powder (AP) can be usefully employed for the production of aerated building elements based on ettringite. Two binary (M1, M2) and one ternary (M3) mixtures, hydrated at 55 °C and 70 °C for curing periods ranging from 2 hours to 28 days, were investigated. The M1 and M2 systems were based on AP and FBC bottom- or FBC fly-ash, M3 on AP and both FBC residues. It has been found that: (i) ettringite easily forms at both 55 ° and 70 °C for all the investigated mixtures; (ii) the M2 system exhibits the largest formation rate and concentration of ettringite (at 70 °C after 2 days of curing), mainly due to the intrinsic good reactivity of FBC fly-ash. The particularly satisfactory results obtained with the M2 mixture encourage to extend the research activity towards the evaluation of the technological and physical properties (e.g. mechanical behaviour and insulating characteristics) of the building elements here synthesized

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