



## Flue gas desulfurization gypsum and coal fly ash as basic components of prefabricated building materials

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### ABSTRACT

The manufacture of prefabricated building materials containing binding products such as ettringite ( $6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$ ) and calcium silicate hydrate (CSH) can give, in addition to other well-defined industrial activities, the opportunity of using wastes and by-products as raw materials, thus contributing to further saving of natural resources and protection of the environment.

Two ternary mixtures, composed by 40% flue gas desulfurization (FGD) gypsum or natural gypsum (as a reference material), 35% calcium hydroxide and 25% coal fly ash, were submitted to laboratory hydrothermal treatments carried out within time and temperature ranges of 2 h–7 days and 55–85 °C, respectively. The formation of (i) ettringite, by hydration of calcium sulfate given by FGD or natural gypsum, alumina of fly ash and part of calcium hydroxide, and (ii) CSH, by hydration of silica contained in fly ash and residual lime, was observed within both the reacting systems. For the FGD gypsum-based mixture, the conversion toward ettringite and CSH was highest at 70 °C and increased with curing time. Some discrepancies in the hydration behavior between the mixtures were ascribed to differences in mineralogical composition between natural and FGD gypsum.

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### 1. Introduction

The use of waste materials and industrial by-products in the manufacture of Portland and blended cements, ordinary and lightweight concrete as well as precast construction products is a research theme of indisputable relevance (Asokan et al., 2009; Bernardo et al., 2007; Bravo and De Brito, 2012; Correia et al., 2011; Gäbel and Tillman, 2005; Huntzinger and Eatmon, 2009; Pelisser et al., 2012; Wattanasiriwech et al., 2009). In particular, coal fly ash and flue gas desulfurization (FGD) gypsum are worthy of consideration because they are generated in huge amounts and are utilized to a still unsatisfactory extent (Ahmaruzzaman, 2010; Balsamo et al., 2010, 2011, 2012; Guan et al., 2011; Marroccoli et al., 2010; Montagnaro and Santoro, 2009). While the former is chiefly used in the cement and concrete industry due to its pozzolanic behavior and suitable particle size distribution, the latter can replace natural gypsum in its main applications (Taylor, 1997). Fly ash is also used in place of natural sand for the manufacture of building materials such as sand-lime bricks and other autoclaved products (Chindaprasirt and Pimraksa, 2008; Cicek and Tanriverdi, 2007; Goñi et al., 2003), precast (Mehta and Monteiro, 2006; Naik et al., 2004; Neville, 2000) and aerated (Kurama et al., 2009; Narayanan and Ramamurthy, 2000) concrete, whose engineering

properties are mainly regulated by binding products, mostly calcium silicate hydrate (CSH), rapidly generated by hydrothermal reactions. Moreover, calcined natural or chemical gypsum, subjected to a proper accelerated curing, can be a basic component of prefabricated lightweight building elements (Sampson, 2011), commonly used in indoor applications where their water solubility is not detrimental.

As substitutes for many of the above-mentioned building materials, ettringite based components (Azuma and Ichimaru, 1976; Azuma et al., 1976; Beretka et al., 1987, 1991) can find useful applications. 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 compound characterized by low density, water insolubility, satisfactory mechanical strength and fire resistance (Manzano et al., 2012; Renaudin et al., 2010; Santoro et al., 1984, 1986). During the early hydration of Portland cement,  $6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$  is generated to a limited extent from the reactions of gypsum (or anhydrite) with calcium aluminates and water (Taylor, 1997). Ettringite can play a more important role as main hydration product of calcium sulfoaluminate ( $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$ ) cement or calcium aluminate cement – calcium sulfate blends (Bernardo et al., 2006; Buzzi et al., 2010; Cuberos et al., 2010; Fernández-Carrasco and Vázquez, 2009; Pace et al., 2011; Scrivener, 2003; Winnefeld and Lothenbach, 2010). Micro- and macro- crystalline ettringite particles are respectively responsible for an expansive behavior and a high mechanical strength; by regulating microstructure and formation rate of ettringite, shrinkage-compensating, self-stressing or

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rapid-hardening cements can be obtained (Gastaldi et al., 2011; Valenti et al., 2012). Hydrating sources of sulfates and oxides or hydroxides of calcium and aluminum are able to produce ettringite (Bernardo et al., 2004; Montagnaro et al., 2003, 2005, 2009; Santoro et al., 1984, 1986); generally, the reaction at room temperature is rather slow and higher curing temperatures are required to promote the ettringite generation. Furthermore, if silica is available in the reacting systems, CSH can be produced; its formation rate (favored by calcium sulfate) is also enhanced by the increase of the reaction temperature (Beretka et al., 1994; Cioffi et al., 1992; Değirmenci, 2008; Kumar, 2000; Marinkovic and Kostic-Pulek, 2007; Min et al., 2008; Shen et al., 2007).

On the basis of the above mentioned considerations, it seemed interesting to (i) carry out a research on the combined use of two by-products coming from the same industrial activity and (ii) undertake an investigation on hydrothermal reactions within a FGD gypsum – fly ash – hydrated lime mixture aimed at obtaining binding products such as ettringite and CSH. The former can be generated by reaction of  $\text{Al}_2\text{O}_3$  contained in fly ash with  $\text{CaSO}_4$  of FGD gypsum and part of hydrated lime; the latter can be formed by combination of residual lime with  $\text{SiO}_2$  given by fly ash. It is important to observe that building materials based on ettringite and CSH, differently from gypsum products, have the potential to be used also in wet conditions, if sulfates given by raw materials are consumed in the formation of water-insoluble ettringite (Beretka et al., 1994). This paper reports the results obtained with the aforesaid mixture and a ternary reference system containing natural gypsum instead of FGD gypsum, hydrated at curing temperatures and times up to 85 °C and 7 days, respectively.

## 2. Experimental

### 2.1. Materials and characterization techniques

As components of the hydrating mixtures, natural gypsum, FGD gypsum, and fly ash (whose composition is given in Table 1) as well as calcium hydroxide (AR-grade) were used. Natural gypsum, together with Portland clinker and natural pozzolan utilized for the pozzolanicity test mentioned below, was supplied by a local cement factory. FGD gypsum and fly ash came from the ENEL power plant of Cerano (Brindisi, Italy) and were given by the ENEL Research Centre of Tutturano (Brindisi, Italy). From the results reported in Table 1, it appears that natural and FGD gypsum had a quite similar chemical composition, also in terms of minor constituents among which Mg and Si oxides, both in the range 3–4%, were the most important. On the other hand, fly ash showed a

definite silico-aluminous nature, and the presence, in non-negligible amounts, of Fe (8.4%), Ca (4.3%) and Mg (2.1%) oxides. The loss on ignition at 950 °C of both gypsums (around 22–25%) was mainly due to bound water and calcium carbonate; that of fly ash (6.5%) was only related to unburnt carbon, being equal to the loss on ignition at 550 °C.

The chemical composition of the raw materials was evaluated by X-ray fluorescence analysis using a BRUKER Explorer S4 apparatus.

Natural and FGD gypsum as well as fly ash were also characterized through X-ray diffraction (XRD) analysis by means of a RIGAKU 2200 diffractometer operated between 5° and 60°  $2\theta$  (Cu  $K\alpha$  radiation). The related diffractograms are shown in Figs. 1–3 where peak intensities are measured in counts per second. The main crystalline phases were (i) gypsum and calcite for natural gypsum, (ii) gypsum, anhydrite and calcite for FGD gypsum, and (iii) quartz, mullite and hematite for fly ash.

Moreover, XRD analysis was employed for investigating the hydrated systems in addition to differential thermal analysis (DTA) carried out with a NETZSCH TASC 414/3 thermoanalyzer with a heating rate of 10 °C  $\text{min}^{-1}$  up to 550 °C.

### 2.2. Pozzolanicity test, proportioning and handling of mixtures

In order to evaluate the fly ash reactivity, a pozzolanicity test was carried out. This test must be performed on blended pozzolanic cements and gives an indication of the suitability of a pozzolanic addition to be used in mixture with Portland clinker and gypsum. The pozzolanicity is assessed by comparing the concentration of calcium ion expressed as calcium oxide present in the aqueous solution (in contact with the hydrated cement for 8 days at 40 °C) with the quantity of calcium ion capable of saturating a solution of the same alkalinity. The pozzolanic cement (and the related pozzolanic addition) is considered to satisfy the test if the concentration of calcium ion in the solution is lower than the saturation concentration. Two pozzolanic cements were prepared for the pozzolanicity test. They were composed by 51% Portland clinker, 45% pozzolanic addition (natural pozzolan or fly ash) and 4% gypsum, ground in a laboratory mill to a Blaine fineness equal to 380  $\text{m}^2 \text{kg}^{-1}$ . Twenty grams of each cement were added to 100 ml of water and, at the end of the accelerated curing,  $\text{OH}^-$  and  $\text{Ca}^{++}$  concentrations were measured.

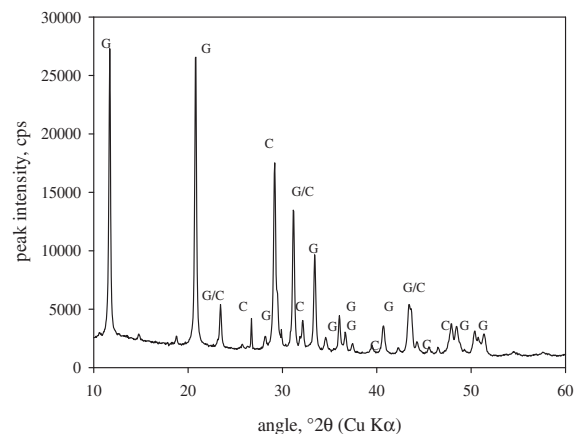
Two mixtures (*Mix1* and *Mix2*), whose composition is indicated in Table 2, were prepared. *Mix1* was composed by 40% natural gypsum, 35%  $\text{Ca}(\text{OH})_2$  and 25% fly ash. In *Mix2* FGD gypsum was used instead of natural gypsum. The mix proportions of each component

**Table 1**  
Chemical composition of natural gypsum, FGD gypsum and fly ash, mass%.

	Natural gypsum	FGD gypsum	Fly ash
$\text{SO}_3$	36.20	36.90	0.77
CaO	30.10	31.90	4.34
MgO	3.66	3.80	2.06
$\text{SiO}_2$	3.00	3.30	48.48
$\text{Al}_2\text{O}_3$	0.85	1.00	24.44
$\text{Fe}_2\text{O}_3$	0.25	0.30	8.43
$\text{TiO}_2$	0.04	0.05	1.08
$\text{P}_2\text{O}_5$	0.01	0.01	0.77
$\text{Mn}_3\text{O}_4$	–	–	0.05
$\text{Na}_2\text{O}$	–	–	1.22
$\text{K}_2\text{O}$	–	–	1.86
l.o.i. <sup>a</sup>	24.60	22.40	6.50
l.o.i. <sup>b</sup>	–	–	6.50
Total	98.71	99.66	100.00

<sup>a</sup> loss on ignition at 950 °C.

<sup>b</sup> loss on ignition at 550 °C.



**Fig. 1.** XRD pattern for natural gypsum: G = gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), C = calcite ( $\text{CaCO}_3$ ).

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