

BY-PRODUCTS FROM PULVERIZED COAL-FIRED POWER PLANTS AS RAW MATERIALS FOR THE MANUFACTURE OF PREFORMED BUILDING COMPONENTS

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Abstract

Hydrothermal reactions among lime, silica, alumina and calcium sulfate are of interest for the production of preformed building components, due to the generation of binding products such as calcium silicate hydrate (CSH) and ettringite ($6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$). Coal fly ash and flue gas desulfurization (FGD) gypsum can be used together with lime as suitable raw materials for the manufacturing process. A laboratory investigation on the hydration behaviour of two ternary systems containing 35% calcium hydroxide, 25% fly ash and 40% FGD gypsum or natural gypsum (as a reference material) was carried out using X-ray diffraction and differential thermal analyses as main characterization techniques. The amounts of the constituents of both mixtures were nearly stoichiometric for the formation of ettringite and a calcium silicate hydrate with a CaO/SiO_2 molar ratio equal to 1.5. Water/solid mass ratio was 0.75. Curing temperatures and times were 55°, 70°, 85°C, and 1, 3, 7 days, respectively. Shorter hydration periods (2, 4, 8 and 16 hours) at 85°C were also investigated. Both ternary blends showed a useful hydration behaviour. At each temperature, the curing length favorably influenced the conversion towards ettringite and CSH, the formation rate of the former being higher than that of the latter. For the natural gypsum-based mixture, the conversion to both reaction products increased with the increase of the curing temperature and the hydration was already started at 85°C and 2 hours of aging. For the FGD gypsum-based mixture, 70°C was the optimum temperature and the maximum conversion was lower than that of the system containing natural gypsum. This behaviour was ascribed to the different composition between natural and FGD gypsum.

Introduction

Coal fly ash and flue gas desulfurization (FGD) gypsum are industrial by-products generated in huge amounts and utilized to a still unsatisfactory extent. The former is chiefly used in the cement and concrete industry due to its pozzolanic behaviour and suitable particle size distribution [1-3]. The latter, like all the "chemical" gypsums, can replace natural gypsum in its main applications, namely as plaster of Paris (if calcined) [4] and set retarder for portland cement [5].

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 [6-11], precast [12-16] and aerated [17-20] concrete, whose engineering properties are mainly regulated by binding products, mostly calcium silicate hydrates (CSH), rapidly generated by hydrothermal reactions.

Moreover, calcined natural or chemical gypsum, subject to a proper accelerated curing, can be a basic component of prefabricated lightweight building elements [21], commonly used in indoor applications where their water solubility is not detrimental.

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 [22-26]. 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 [5]. Ettringite can play a more important role as main hydration product of calcium sulfoaluminate ($4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$) cements [27] or calcium aluminate cement – calcium sulfate blends [28-29]. Micro- and macro- crystalline ettringite particles are respectively responsible for an expansive behaviour and a high mechanical strength; by regulating microstructure and formation rate of ettringite, shrinkage-compensating, self-stressing or rapid-hardening cements can be obtained [24; 30-36].

Hydrating mixtures, containing gypsum and oxides or hydroxides of calcium and aluminum, are able to produce ettringite [37-39]; 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, a calcium silicate hydrate can be produced; its formation rate (favored by calcium sulfate) is also enhanced by the increase of the reaction temperature [40-49].

The aim of this research is to investigate the hydrothermal reactions within a ternary blend composed by a mixture of fly ash and FGD gypsum (coming from the same coal-fired power plant) with hydrated lime, with the purpose of converting the reactants into binding products such as ettringite and CSH. The former can be generated by the reaction of Al_2O_3 contained in the fly ash with CaSO_4 of the FGD gypsum and part of the hydrated lime; the latter can be formed by combination of the residual lime with SiO_2 given by the fly ash. It is interesting to observe that building materials based on CSH and ettringite, differently from gypsum products, have the potential to be used also in wet conditions, if sulfates given by the raw materials are consumed in the formation of water-insoluble ettringite [49].

Preliminary results obtained with the above-mentioned ternary system and a reference mixture containing natural gypsum instead of FGD gypsum, hydrated at curing temperatures and times up to 85°C and 7 days, respectively, are here described. Afterwards, the investigation will be extended to systems containing gypsum in a calcined form and portland cement in partial replacement of hydrated lime, in order to exploit also the strength contribution given by the rapid setting of calcined gypsum and the early hydration of portland cement [41; 45; 47-49].

Experimental

Materials

As components of the hydrating mixtures, natural gypsum, fly ash and FGD gypsum (whose composition is given in Table 1) as well as calcium hydroxide (Analytical Reagent) 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. Fly ash and FGD gypsum came from the ENEL power plant of Cerano (Brindisi, Italy) and were given by the ENEL Research Centre of Tutturano (Brindisi, Italy).

The loss on ignition at 950°C of both gypsums was mainly due to bound water and calcium carbonate; that of fly ash was only related to the unburnt coal, being equal to the loss on ignition at 550°C .

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

	<i>natural gypsum</i>	<i>fly ash</i>	<i>FGD gypsum</i>
<i>SO₃</i>	36.20	0.77	36.90
<i>CaO</i>	30.10	4.34	31.90
<i>MgO</i>	3.66	2.06	3.80
<i>SiO₂</i>	3.00	48.48	3.30
<i>Al₂O₃</i>	0.85	24.44	1.00
<i>Fe₂O₃</i>	0.25	8.43	0.30
<i>TiO₂</i>	0.04	1.08	0.05
<i>P₂O₅</i>	0.01	0.77	0.01
<i>Mn₃O₄</i>	-	0.05	-
<i>Na₂O</i>	-	1.22	-
<i>K₂O</i>	-	1.86	-
<i>l.o.i.</i> ^a	24.60	6.50	22.40
<i>l.o.i.</i> ^b	-	6.50	-
Total	98.71	100.00	99.66

^a loss on ignition at 950°C

^b loss on ignition at 550°C

Fly ash and FGD gypsum were characterized by means of X-ray diffraction (XRD) analysis. The related diffractograms are shown in Figure 1: XRD peak intensity was measured in counts per second (cps).

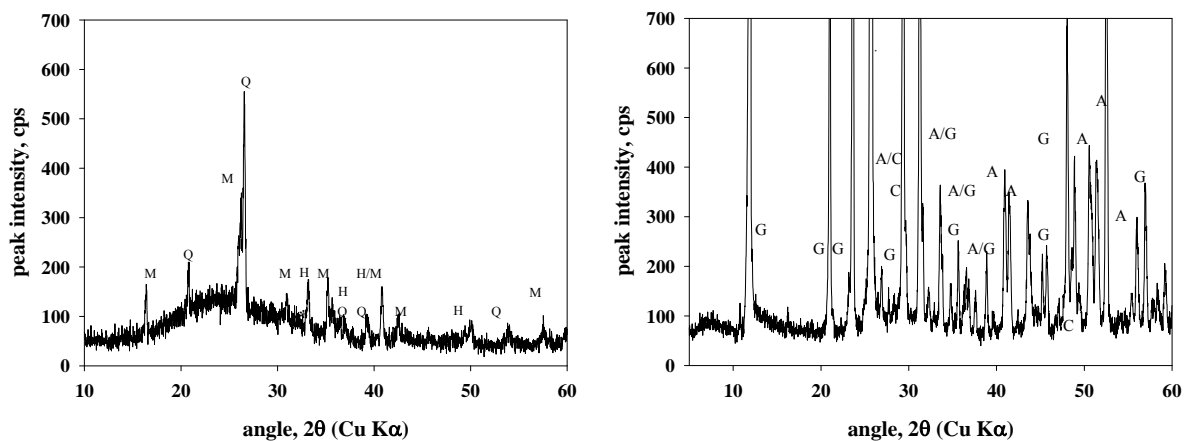


Figure 1. XRD patterns for fly ash (left) and FGD gypsum (right): Q=quartz (SiO_2), M=mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), H=hematite (Fe_2O_3), G=gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), A=anhydrite (CaSO_4), C=calcite (CaCO_3).

The main crystalline phases were quartz, mullite and hematite for the fly ash and gypsum, anhydrite and calcium carbonate for the FGD gypsum.

Test procedures, mix formulation and characterization techniques

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 m²/kg. Twenty grams of each cement were added to one hundred millilitres of water and, at the end of the accelerated curing, OH⁻ and Ca⁺⁺ concentrations were measured.

The chemical composition of natural gypsum, fly ash and FGD gypsum was evaluated through X-ray fluorescence analysis by using a BRUKER Explorer S4.

Two mixtures (Mix1 and Mix2), whose composition is indicated in Table 2, were prepared.

Table 2. Composition of the ternary mixtures, mass %.

	<i>Ca(OH)₂</i>	<i>natural gypsum</i>	<i>fly ash</i>	<i>FGD gypsum</i>
<i>Mix1</i>	35	40	25	-
<i>Mix2</i>	35	-	25	40

The mix proportions of each component were nearly the stoichiometric amounts required by the formation of ettringite and calcium silicate hydrate: it was assumed that (i) CaSO₄ and Al₂O₃ (given by gypsum and fly ash, respectively) reacted to give only ettringite and (ii) SiO₂ contained in the fly ash was exclusively involved in the formation of a calcium silicate hydrate with a CaO/SiO₂ molar ratio equal to 1.5.

Mix1 and Mix2 were paste hydrated with a water/solid mass ratio equal to 0.75. The pastes, shaped as cylindrical discs (15 mm high, 30 mm in diameter), were cured in a thermostatic bath at 55°, 70° and 85°C for 1, 3 and 7 days; shorter hydration times (2, 4, 8 and 16 hours) at 85°C were also investigated. At the end of each aging period, the samples were ground under acetone (to stop hydration), then treated with diethyl ether (to remove water) and stored in a desiccator over silica gel-soda lime (to ensure protection against H₂O and CO₂).

XRD analysis was employed for characterizing fly ash and FGD gypsum, as well as investigating the hydrated systems together with differential thermal analysis (DTA). A RIGAKU 2200 diffractometer, operating between 5° and 60°2θ (Cu Kα radiation), and a NETZSCH TASC 414/3 thermoanalyzer with a heating rate of 10°C/min from 20° to 1000°C were used.

Results and Discussion

The fly ash used in this investigation showed a reactivity similar to that of a natural pozzolan usually employed for the pozzolanic cement manufacture. As a matter of fact, both fly ash and natural pozzolan satisfied the pozzolanicity test inasmuch as the representative points of the related cements are located below the saturation curve (Figure 2).

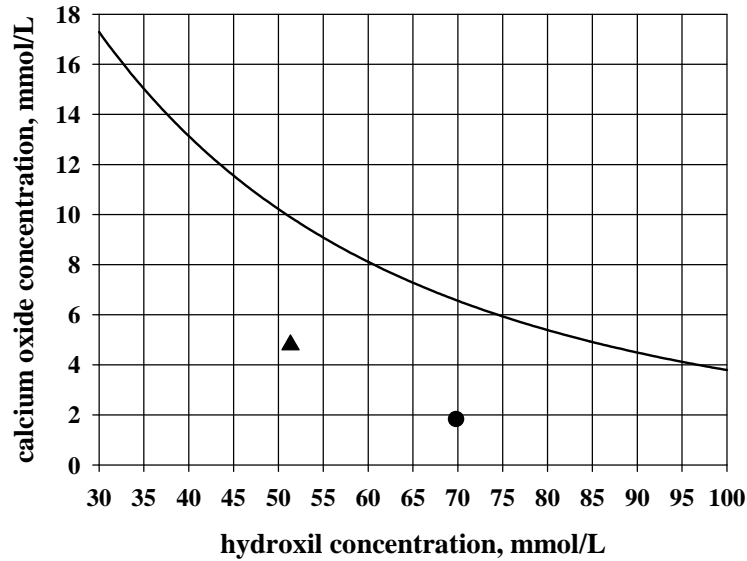


Figure 2. Saturation curve at 40°C (●, natural pozzolan-based cement; ▲, fly ash-based cement).

Figures 3, 4 and 5 illustrate the DTA thermograms of Mix1 and Mix 2 cured for 1, 3 and 7 days at the temperatures of 55°, 70° and 85°C, respectively.

Hydration products such as ettringite and calcium silicate hydrate, CSH type I according to Taylor [5], as well as unreacted gypsum and calcium hydroxide can be easily detected. Their identification was made on the basis of literature data [5; 50-52]. In particular, CSH-I, ettringite, gypsum and calcium hydroxide were individuated through endothermic peaks at $95^{\circ}\pm 27^{\circ}\text{C}$, $127^{\circ}\pm 22^{\circ}\text{C}$, $173^{\circ}\pm 13^{\circ}\text{C}$ and $495^{\circ}\pm 10^{\circ}\text{C}$, respectively.

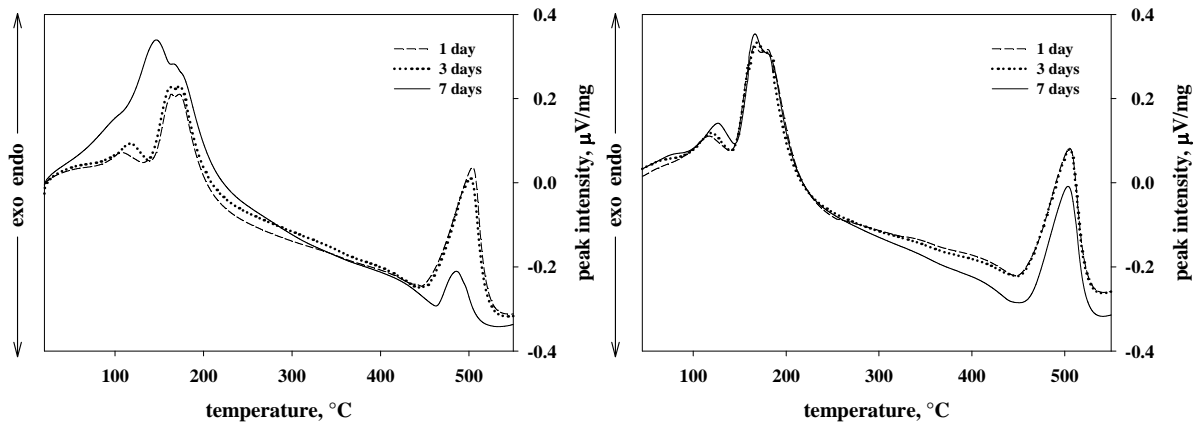


Figure 3. DTA thermograms of Mix1 (left) and Mix2 (right) hydrated for 1, 3 and 7 days at 55°C.

At 55°C, for Mix1, the hydration proceeded slowly up to 3 days of curing, while a satisfactory conversion towards ettringite was attained only after 7 days when the CSH signal was also detected; for Mix2, the reactions developed to a limited extent during all the investigated time period (Figure 3).

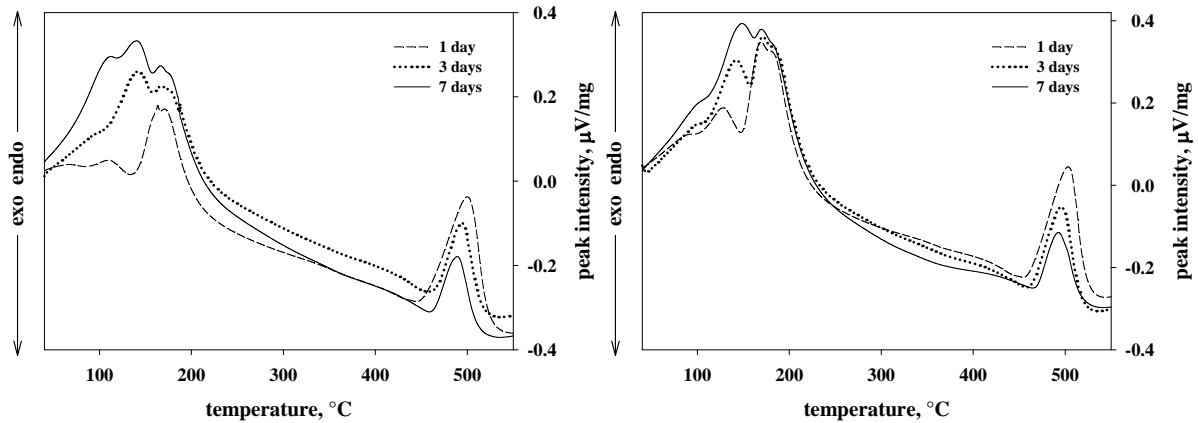


Figure 4. DTA thermograms of Mix1 (left) and Mix2 (right) hydrated for 1, 3 and 7 days at 70°C.

Compared to the previous temperature, Mix1 and Mix2 showed at 70°C a steady increase of the formation rate of both hydration products (Figure 4): the CSH effect was already evident at 1 day of curing and quite significant at 7 days, especially for Mix1.

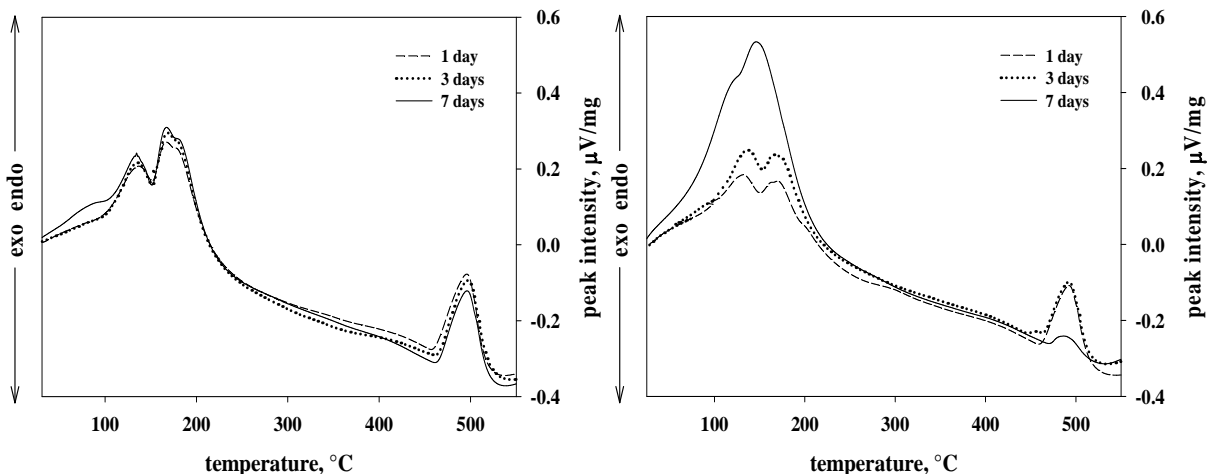


Figure 5. DTA thermograms of Mix1 (left) and Mix2 (right) hydrated for 1, 3 and 7 days at 85°C.

At 85°C (Figure 5), for Mix1, a further enhancement of the hydration progress was observed, particularly at 7 days of curing when the calcium hydroxide peak was strongly reduced and that of gypsum was completely included into the ettringite signal; for Mix2, on the other hand, the formation rate of ettringite and CSH was lower than that attained at 70°C; nevertheless, it is higher than the formation rate of both hydration products at 55°C. The occurrence of an optimum temperature at about 70°C for Mix2 can be related to: (i) the peculiar FGD gypsum composition containing calcium sulfate as both anhydrite and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and (ii) the difference in the water solubility and its temperature dependence between the two forms of calcium sulfate. Finally, it has to be pointed out that, for both Mixes at all the investigated curing temperatures, the formation rate of CSH is quite lower than that of ettringite.

The particularly good results reached at 85°C for Mix1 suggested to extend the investigation to curing periods shorter than 1 day at the same temperature.

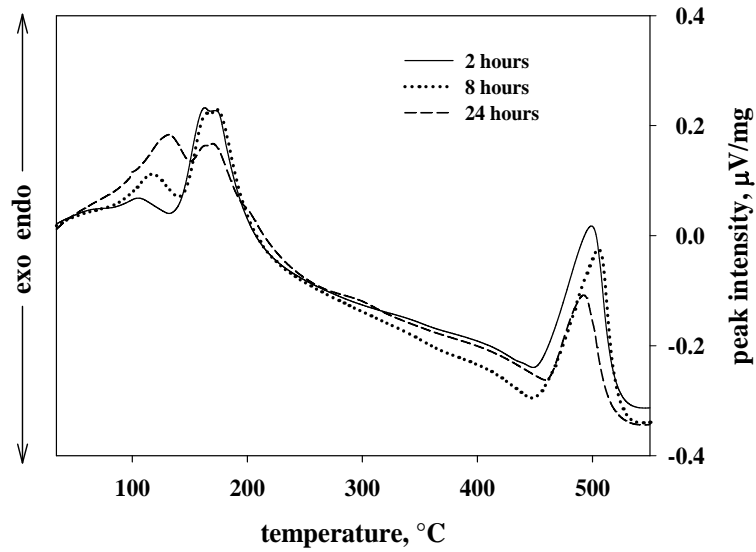


Figure 6. DTA thermograms of Mix1 hydrated for 2, 8 and 24 hours at 85°C.

Mix1 exhibited an evident reactivity already at 2 hours, as shown in Figure 6 where, for the sake of comparison, the thermogram at 1 day of curing is also reported.

The XRD data on the hydrated systems substantially agree with the DTA results; as an example, the diffractogram of Mix1 cured at 85°C for 7 days is illustrated in Figure 7: for

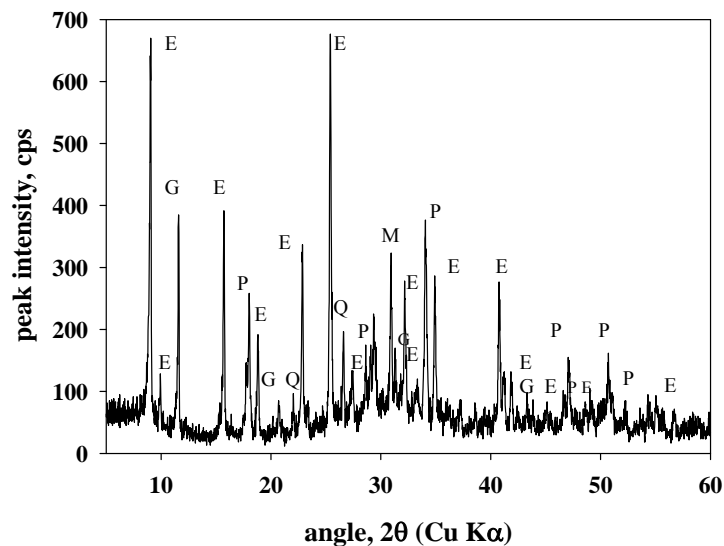


Figure 7. XRD pattern for Mix1 hydrated at 85°C for 7 days: E=ettringite ($6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$), P=portlandite ($\text{Ca}(\text{OH})_2$), G=gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), M=mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), Q=quartz (SiO_2).

ettringite and calcium hydroxide, strong and weak signals were respectively observed and residual gypsum as well as unreacted phases belonging to fly ash, such as quartz and mullite, were also present.

Conclusions

Both coal fly ash and flue gas desulfurization (FGD) gypsum have the potential to be used in application fields different from the cement, concrete and gypsum industries which represent well-established utilization sectors. In order to enhance the exploitation of these industrial by-products, the manufacture of preformed building components based on binding products such as calcium silicate hydrate and ettringite was explored. Two hydrating ternary systems consisting of 35% calcium hydroxide, 25% fly ash and 40% natural or FGD gypsum were investigated. The mix proportions of each component were nearly the stoichiometric amounts required by the formation of ettringite and a calcium silicate hydrate with a lime/silica molar ratio equal to 1.5. Hydrothermal reactions among lime, calcium sulfate (contained in gypsum), silica and alumina (both given by fly ash) carried out at curing temperatures and times up to 85°C and 7 days, respectively, were followed by XRD and DTA analyses. Both blends showed a useful hydration behaviour. It has been found that a treatment performed at 70°C for 7 days promotes a significant generation (higher for the system containing natural gypsum) of ettringite and calcium silicate hydrate. At each curing temperature and time, the formation rate of ettringite was higher than that of calcium silicate hydrate. Compared to the results obtained at 70°C, a natural gypsum-based mixture was able to enhance its hydration properties when cured at a higher temperature (85°C); on the other hand, the FGD gypsum-based mixture showed a worse behaviour when the operating conditions were changed. These phenomena can be related to the difference in the water solubility and its temperature dependence between natural and FGD gypsum, being the former composed by calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and the latter by both anhydrite (CaSO_4) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Further research is needed for improving the hydration behaviour of the investigated systems through the choice of suitable operating conditions including also the proportioning of the mix constituents.

Acknowledgements

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