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The effect of natural pozzolan on delayed ettringite formation of the heat-cured mortars

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HIGHLIGHTS

- The use of finer pozzolan in partial replacement of cement controlled or even eliminated the DEF expansion.
- The substitution of cement with coarse pozzolan is not only ineffective but even accelerated the DEF expansion.
- The DEF was correlated with the evolution of the mass, compressive strength, elastic modulus and porosity of the specimens.

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ABSTRACT

Delayed Ettringite Formation (DEF) is an internal sulfate attack caused by early age heating to a temperature of over 70 °C. In this paper, the effect of natural Algerian pozzolan on the expansion of cement mortars caused by DEF was investigated. For this purpose, a portion of cement was replaced by natural pozzolan, with three different dosages (10%, 20% and 30%) and finenesses (fine, medium, and coarse). The results obtained highlighted the significant effects of natural pozzolan on DEF and the correlation existing between the expansion of the heat-cured mortars and the evolution of their mechanical properties.

1. Introduction

Delayed Ettringite Formation (DEF) is an internal sulfate attack caused by heat-induced decomposition of ettringite formed during the initial hydration of cement at elevated temperature (above about 70 °C) and its re-crystallization in the hardened matrix [1–3]. This reaction is a physico-chemical phenomenon inducing an expansion of the cement paste that could lead to cracking of concrete. These cracks result in a decrease of the mechanical performances and durability parameters of the material. Highlighted in the middle of 1980s, this pathology exists in most parts of the world and has become one of the major problems for the durability of concrete structures and precast concrete elements, causing significant and costly damages.

The use of pozzolanic additives in partial substitution of cement may be an efficient way to prevent concrete from internal sulfate attack. Indeed, pozzolanic reactions enable to reduce the amount of calcium hydroxide in the material, improving the sulfate resistance of the material [4]. Ramlochan et al. [5] showed that the use of silica fume in replacement of cement by up to 8% did not control the long-term expansion related to DEF. However, the beginning of the expansion was delayed due to the low permeability of mortars incorporating silica fume. Besides, the use of a small proportion (8%) of metakaolin could prevent the long-term expansion related to DEF. This was attributed to the high content of Al_2O_3 in metakaolin and the effect of the reduction leaching of the alkali hydroxide from the pore fluid. Indeed, the microstructure was showed that the outer C–S–H gel appeared less fibril and the cement matrix was less porous at earlier ages with use of metakaolin or silica fume. The microanalytical evidence suggests that monosulfate was finely intermixed with the C–S–H gel in the outer product at the end of the heat treatment. In specimens that expanded during moist storage at ambient temperature this monosulfate was replaced by ettringite, which initially formed also on a fine scale intermixed with the C–S–H gel in the outer product. With the incorporation of a sufficient amount of an Al_2O_3-bearing mineral admixture this did not appear to occur. For fly ash, the

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quantity required to eliminate the expansion depends on its composition. Fly ash with a low concentration in lime seems to work better with low rates of substitution (15–25%) while fly ash with a high concentration in lime could be effective at higher replacement levels (25–35%). For blast furnace slag, the substitution rate needed to eliminate the long-term expansion with the majority of the cements was about 25%, but higher levels may be required for cements with very high sulfate or alkali contents. More recently, according to data recorded on 12-month specimens, Atahan and Dikme [4] reported that different mineral additives, including nano (colloidal) silica, micro silica, fly ash and ground granulated blast furnace slag showed a significant mitigation of expansion due to internal sulfate attack. Particularly, the efficiency of nanosilica in limiting the expansions caused by internal sulfate attack was found to be highly significant when used in very low substitution rate of cement (4–6%). This result can be attributed to both its very high surface area (>80,000 m^2/kg) and purity (>99% SiO_2).

Moreover, the technical guide [6] for the prevention of disorders due to delayed ettringite recommends to use cements with low heat of hydration in accordance with standard NF EN 197-1/A1, such as blended cements (CEM II to CEM V) or binary binders prepared with CEM I and pozzolanic additions.

Nevertheless, there are still very few studies on the effects of natural pozzolanic additions on the development of DEF. In this context, the experimental study presented in this paper focuses on characterizing the influence of the fineness and dosage of natural pozzolan and the effects of the storage conditions of mortars on the risk of occurrence of DEF.

2. Experimental study

2.1. Materials and experimental program

The cement used in this study was a CEM I 52.5 N CE CP2 NF from Couvrot plant (France). The volcanic tuft used for this study was an Algerian natural pozzolan, extracted from the Bouhamidi deposit in the Beni-Saf region (north-west of Algeria). The volcanic tufts were received in rock form and were crushed to obtain three different finenesses (fine pozzolan: PzF, medium pozzolan: PzM and coarse pozzolan: PzC). 0/2-mm siliceous sand with a density of 2600 kg/m^3 was used for the preparation of mortars. This sand meets standard NF EN 196-1 specifications [7] and is classified as non-reactive with respect to alkali-silica reaction (standard NF-P 18-590 [8]). Siliceous sand was chosen because it leads to faster expansion than limestone sand [9].

The mortars were prepared according to NF EN 196-1 standards [7], with three different pozzolan dosages (10%, 20% and 30%). Considering the binder content as the sum of cement and pozzolan dosages, each mortar was mixed with a binder/sand weight ratio (B/S) of 1/3 and a total water/binder ratio (W_t/B) of 0.56. Their composition is detailed in Table 1. The amount of added water in Table 1 corresponds to the mass of mixing water directly introduced in the mixer bowl, whereas the amount of total water takes into account both the mass of mixing water and the natural water content of pozzolan. In order to accelerate and amplify the appearance of expansion, 3.1% (by weight of binder) of sodium sulfate (Na_2SO_4) were added to the mortars [10,11]. It was dissolved in the mixing water before introduction in the mixer bowl.

Mortars were cast under the form of $40 \times 40 \times 160$ mm^3 prisms in steel moulds, equipped with brass studs to measure the specimen expansion. The moulds were thus readily covered with a plastic plate to prevent evaporation and the mortars were submitted to a four-stage heat treatment (Fig. 1). They were initially cured for 2 h at 20 °C. The temperature was then increased to 80 °C at a rate of 30 °C per hour. The temperature was maintained at 80 °C for 10 h, and finally decreased during 11 h to reach 20 °C. Thermocouples were placed in the oven, at the center and the edge of the sample to record the temperatures reached during the treatment.

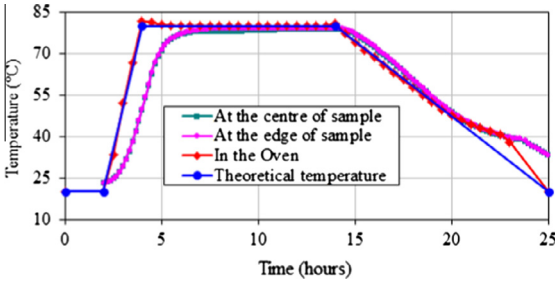

Fig. 1. Heat treatment applied to the mortar samples.

The specimens were then removed from the moulds and stored in closed tanks containing deionised water at 20 °C. Two storage conditions were considered. In the first case (denoted "NRW": Non-Renewed Water), the bath water was not renewed during the whole period test. In the second case (denoted "RW": Renewed Water), the water was regularly renewed: it was changed weekly up to 8 weeks; then; every 2 weeks up to 24 weeks and finally every 4 weeks until the end of the test period.

2.2. Testing methods

The particle size distribution of the materials was measured using laser diffraction with a CILAS 1180L apparatus. XRD patterns were done by using an X-ray diffractometer SEIFERT MZ VI E with Co Kα radiation. Measures were done on the bulk powdered samples.

The pozzolanic activity was determined by the method of $Ca(OH)_2$ depletion in lime–pozzolan paste [12,13]. This method is based on the decomposition of crystalline calcium hydroxide into calcium oxide and water in a temperature range from 400 °C to 600 °C by thermogravimetric analysis (TGA). Lime–pozzolan paste was performed by combining 50% natural pozzolan and 50% $Ca(OH)_2$ powder in presence of enough water to give a normal consistency paste. The fresh pastes were filled into the plastic bottles to prevent moisture loss and carbonation, and then the bottles were stored in the room at 20 °C and at relative humidity of 50%. The amount of reacted lime in the lime–pozzolan pastes for a specific age (7 and 28 days), was calculated from the difference between the initial and the final amount of free lime that was determined by a TGA/DSC1 device of Mettler Toledo company in a static air nitrogen with heating rate 5 °C/min from 25 °C to 800 °C. Before to realize the TGA and to accelerate the pozzolanic reaction, the paste bottles were cured at 50 °C for 24 h. The pozzolanic activity is expressed as percent of the ratio of reacted lime amount to initial lime amount.

The evolutions of length, mass, elastic dynamic modulus and compressive strength of the specimens were measured over a test period of more than 450 days.

The length and mass measurements were performed in the air using an extensometer and a balance with a resolution of ±1 μm and ±0.01 g, respectively. The first measurements were carried out 24 h after the casting. For each mortar and for each curing condition, the average expansion and the mass variation were obtained from three different specimens. These specimens were then used to determine the dynamic Young's modulus (E_{dyn}) and the compressive strength (R_c) of each mortar. E_{dyn} was measured by non-destructive impulse excitation tests using a Grindosonic® apparatus. The mortar prisms were elastically struck at half length. The flexural and torsional resonant frequency of the productive signal were recorded by a vibration sensor. Finally, E_{dyn} is determined from the frequencies, geometric dimensions

Table 1
Mortar mix proportions.

Reference	Components									
	Cement (g)	PzF (g)	PzM (g)	PzC (g)	Sand (g)	Na_2SO_4 (g)	Water added		Total water	
							Mass (g)	W_a/B	Mass (g)	W_t/B
Ref.	450	–	–	–	1350	13.95	252	0.56	252.00	0.560
PzF30	315	135	–	–					262.46	0.597
PzM10	405	–	45	–					254.73	0.570
PzM20	360	–	90	–					257.47	0.579
PzM30	315	–	135	–					260.20	0.589
PzC30	315	–	–	135					258.34	0.582