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Advanced testing and performance specifications for the cementitious materials under external sulfate attacks

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HIGHLIGHTS

- Development of a monitoring strategy.
- Decoupling of the sulfate attack phenomena.
- Better understanding of micro-degradation mechanism.
- Proposition of new performance indicators.

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ABSTRACT

A new monitoring approach was developed to enhance the analysis of performance tests and provide new sulfate resistance criteria. Even in the case of low degradation rates or non-swelling materials exposed to external sulfate attacks, the method allows detecting microscopic evolutions via a set of easily accessible monitored parameters. The monitoring has been performed on a set of sulfate-resisting and non sulfate-resisting cement-based mortars. The main phenomena induced by external sulfate attack are leaching, precipitation, aggregates loss and cracking. Based on the monitoring of mass, hydrostatic weighing, elongation and the amount of leached OH^- the method provides the samples dimensional variations, the volume and mass changes of minerals and free water, corresponding to the main phenomena of the external sulfate attack. On the one hand, the phenomena decoupling allows a better understanding of the sulfate attack mechanism. The observed equivalence between the volumes of leached and precipitated products highlights the influence of portlandite, the major leached mineral, on the precipitation mechanism. The precipitation-deformation correlation and the samples absolute deformation monitoring showed a common expansion mechanism for the different cement compositions. The cement type was found to influence the magnitude of deformations. On the other hand, the determination of the volume variations corresponding to each phenomenon allows the proposition of new performance indicators from the monitoring approach outputs: the averaged density, the deformation path and the expansion potential. The three indicators were sensitive to the microstructural and macroscopic evolutions. The expansion potential, related to crystallization pressure, was found to depend on cement composition.

1. Introduction

External sulfate attacks are caused by the ingress of sulfate ions from the environment. They result in an increase in porosity, local expansion and cracking. As a consequence the mechanical properties and the durability of cement-based materials are affected [28,23]. Sulfate attacks have been taken into account in the design of concrete mixtures since the 1920s and the first standards on cement. The so-called "sulfate resisting" cements have generally shown good behaviour on site, as very few cases of external sulfate attacks have been reported. However the composition of cements has been changing for the last decades, in order to design more sustainable construction products. Changes in clinker content or chemical composition are likely to affect the sulfate resistance of cement-based materials [14]. A good understanding of the mechanism of degradation, reliable tests, and relevant indicators are thus needed to assess the durability of new cements and concrete exposed to external sulfate attacks.

The mechanism of degradation of cement-based materials is now relatively well known [12,15]. The ingress of external sulfate solution modifies the chemical equilibrium between solid phases

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and interstitial solution in the cementitious matrix [7,10,24]. The increase of sulfate concentration in interstitial solution results in the formation of ettringite (or alumino ferrite trisubstituted AFt) from monosulfoaluminate $2CaO{\cdot}Al_2O_3{\cdot}Ca_2SO_4{\cdot}12H_2O$ (alumino ferrite monosubstituted AFm). Expansion is normally associated to ettringite formation [19,18], even gypsum formation could lead to samples swelling [16]. The theory that is consistent with most of experiments and observations is the crystal growth pressure. The crystal growth theory describes the crystallization pressure produced by supersaturation and confinement [8,9,27]. According to this theory, the driving force for the crystallization pressure is the supersaturation of the pore solution with respect to ettringite. The formation of ettringite does not necessarily result in expansion or damage. This is supported by numerous field observations in the past in which no correlation between the amount of formed ettringite and observed expansion. Significant expansion pressure higher than tensile strength can only be exerted by ettringite which forms in small pores within a certain size range [9], approximately 10–50 nm, depending on the cement used. Microstructural studies [3] showed that penetrating sulfates first react with monosulfate in pockets which does not lead to stress or expansion. On depletion of the pockets content, monosulfate which is finely intermixed in C-S-H then reacts to form expansive ettringite. The scenario of sulfate attack scenario has been confirmed by the zonation observed on damaged samples [1,21]. These experimental results confirmed that sulfate attack do not only cause expansion but also softening and decohesion. The formation of gypsum and ettringite requires a source of calcium. Calcium can be provided by the leaching of portlandite and C-S-H. The leaching of the portlandite and the progressive decalcification of C-S-H cause a softening of cement matrix and a decrease of strength [4].

Performance-based specifications and methodologies of qualification of cement-based materials are often associated to testing procedures. Laboratory conditions should be representative of field exposure. The typical concentration in sulfate-rich environments is 0.02–3 g/L. Concrete structures are partially or fully saturated, or exposed to drying and wetting cycles [9,1,13]. Previous studies have also shown the influence of counter ions, temperature, and pH control. New experimental procedures have been developed to provide more representative sulfate resistance tests [5,22].

Most of performance tests and criteria are based on length measurements and expansion limits (ASTM C 1012, 2000). Expansion data do not provide enough information to assess the chemical reactions and understand the mechanisms causing damage. Moreover, expansion can be caused by other phenomena [29], and the phenomena occurring during the first stage of sulfate attack do not result in significant expansion [21,25].

This paper presents a new monitoring approach aimed at enhancing performance tests and criteria. Based on some relatively accessible monitoring parameters such as mass, leaching, and hydrostatic weighing, we deduced the mass and volume variations associated to chemical changes and cracking to monitor sulfate attack. The results of this analysis were directly used to define new performance indicators to assess the durability of the new construction materials. This new approach could be the way to correlate the chemical and mechanical evolutions and expansion potential related to crystallization pressure development.

2. Experimental program

In order to develop a new sulfate attack monitoring strategy, a double purpose experimental study was designed to understand the scenario of sulfate attack and then find new monitoring parameters to improve existing performance tests and enhance their reliability and relevance.

2.1. Materials and mixtures

The compositions of cements used in the experimental study are given in Table 1. The NSR is a non sulfate resisting cement with a relatively high C_3A content (6.4 %), the two others cements SR5 and SR3 comply with criteria on sulfate resisting cements with relatively low C_3A contents, respectively 0.7 and 0.4%.

A mortar mixture was designed (Table 2) by adapting the composition defined in EN 196 standard. The paste volume, i.e. the sum of water and cement volumes, was kept constant. The water-to-cement ratio was increased from 0.5 to 0.6. French standard sand (SNL, 0.08 mm – 1.6 mm size), according to the norm EN 196-1, was used. It's natural siliceous sand with generally isometric and rounded particles shape [2].

Table 1
Cement compositions.

		CEM I NSR 52.5	CEM I 52.5 SR5 PM	CEM I 52.5 SR3 PM
	Clinker (%)	91.9	92.8	94
Mineralogical composition of clinker	C_3S	67.9	72.9	67.4
	C_2S	13.1	19	16.1
	C_3A	6.4	0.7	0.4
	C_4AF	10.4	6.7	13.7
	Lime/Portlandite	0.8	0.3	1.5
	Alkali sulfates	1.5	0.3	1
Sulfatted additions	Anhydrite	4.4	2.4	1.8
	Bassanite	0.5	0.8	3.3
	Gypsum	0.2	0.9	0.6
Chemical Composition of the cements	PF950	2	1.5	1.4
	SiO_2	19.4	22.4	20.5
	Al_2O_3	5.1	2.9	3.3
	Fe_2O_3	2.9	2.3	5.2
	CaO	63.1	67	64.8
	MgO	1.8	0.8	0.7
	SO_3	3.6	2.3	2.8
	K_2O	0.9	0.2	0.7
	Na_2O	0.2	0.1	0.1
	SrO	0.1	0.1	0
	TiO_2	0.3	0.1	0.2
	P_2O_5	0.3	0.1	0.4
	MnO	0.1	0	0.1
	Cl	0.079	0.027	0.081