Influence of initial material properties on the degradation of mortars with low expansion cements subjected to external sulfate attack

Sonia Boudache, Ahmed Loukili, Emmanuel Rozière, Laurent Izoret

Influence of initial material properties on the degradation of mortars with low expansion cements subjected to External Sulfate Attack

Sonia Boudache [1,2], Ahmed Loukili [1], Emmanuel Rozière [1], Laurent Izoret [2]

Abstract

External sulphate attack consists in reactions between sulphate ions and hydration products causing crystallisation pressures then macroscopic expansion and cracking. The penetration of sulphates within the material is the rate-limiting step. Thus, laboratory tests can last a few years before giving usable results. Moreover some cement-based materials show relatively long latency period and low expansion, hence the need for accelerated testing procedure and/or alternative indicator to shorten the response time. It is possible to shorten the response time by stimulating the penetration of sulphates. This can be achieved by drying the material at 60°C then to saturate it with a sulphate solution. The impact of this thermal pre-conditioning on the sulphate attack phenomenology still remains unclear. In this study, two sulphate-resisting cements, one Portland cement with low-C_3A content (SR3) and a CEM III/B cement, and two blended slag-fly ash cements CEM V were subjected to external sulphate attack. The behaviour of mortars with and without thermal pre-conditioning was analysed. The microstructure of tested specimens was also studied using TGA, Hg- porosimetry, X-ray tomography, and XRD. Pre-conditioning did not influence the chemical properties of formed sulphate-rich phases but modified the microstructure of mortars with different trends depending on cement type. CEM V mortars with pre-conditioning showed finer porosity and lower volumes of precipitation. These modifications of mortar microstructure were consistent with the macroscopic behaviour of mortars with and without thermal pre-conditioning.

Keywords: External sulphate attack, testing procedure, thermal pre-conditioning, blended cement

1. Introduction

External sulphate attack results from the interactions between a sulphate-rich environment, such as sea water and some ground waters, and a cement-based material. When the material is fully immersed, the penetration of sulphate occurs by diffusion. In the case of groundwater, the cementitious structure is

[1] S Boudache . A Loukili .E.Rozière [1]
Institut de Recherche en Génie Civil et Mécanique, GeM, UMR CNRS 6183, Ecole Centrale de Nantes, 1 rue de la Noé, 44321 Nantes, France

e-mail : sonia.boudache@ec-nantes.fr
e-mail : ahmed.loukili@ec-nantes.fr
e-mail : emmanuel.roziere@ec-nantes.fr

[2] Association Technique de l'Industrie des Liants Hydrauliques (ATILH), 7 place de la Défense, 92974 Paris La Défense, France
l.izoret@atilh.fr

partially exposed to water, the capillary suction is the driving force for the penetration of sulphates. The presence of sulphates and their counter-ions in the material leads to a modification of the physical and chemical equilibrium. The mineralogical phases of the cement paste being destabilized, they get dissolved. Ions in solution can react with sulphates to form new compounds which precipitate once saturation concentration is reached. The chemical reactions occurring during external sulphate attack greatly depend of the nature of the hydrates present in the cement paste. The counter-ion of the sulphate salt is also a major parameter [1]. In the case of a sodium sulphate attack, ettringite and gypsum can be formed. The precipitation of ettringite is known to be the cause of expansion and cracking in the material [2]. The crystallization pressure theory [3;4] states two conditions inherent to cracking during the formation of ettringite. The sulpho-aluminate phase must form in a confined environment (pores of diameter lower than 100 nm) and the solution must be supersaturated with regard to ettringite.

The critical part played by ettringite formation in the degradation of cement-based material by sulphates shaped the way laboratory tests have been designed. The most widely used indicator to determine the sulphate resistance is the expansion. In the framework of performance-based specifications for durability, the testing procedure is also expected to shorten the response time by accelerating the degradation and/or defining indicators with better sensitivity. This paper first presents a state of the art of existing procedures used to accelerate external sulphate attacks in laboratory conditions. The accelerated testing procedure designed by Messad et al. [5], based on oven-drying then saturation with sulphate solution under vacuum, is retained. Its main purpose is to provide a comparative performance test for external sulphate attack. Thus, it allows distinguishing sulphate resistant materials from materials prone to expansion.

In this perspective, laboratory tests are a crucial tool to determine the sulphate-resisting character of cements. The most important composition parameters that will make a cement sulphate resisting or not are well anticipated, the first one being the C_3A content. If ettringite is considered the main vector of damage during sulphate attack, the C_3A content of the cement (main source of aluminate for the formation of secondary ettringite) is therefore the main factor making a cement vulnerable to sulphate attack. The lower the clinker C_3A content, the better the cement will resist to sulphate. CEM III and CEM IV cements sulfate-resisting (SR) characteristic partly comes from their lower clinker content. Thus, CEM III and CEM IV cements have less C_3A content. But it is not the only explanation to their SR behaviour. Portlandite (CH) has been proved to have an important part in external sulphate attack. CH leaching brings Ca^{2+} ions available for the precipitation of ettringite. CH dissolution is a fuel for external sulphate attack. Thus, the pozzolanic reactions consuming CH during hydration is cutting this source of ions susceptible to react with sulphate. Moreover, the pozzolanic reactions induce a refinement of porosity thus lower diffusivity. The low clinker content and the pozzolanicity do not only concern CEM IV cements, but also CEM V cements. We can expect that, similarly to CEM IV cements, CEM V cements also being pozzolanic, they could be considered SR. This needs to be confirmed by laboratory tests allowing to distinguish between cements that might not expand in short times. Thus, the pre-conditioning treatment designed by Messad et al. [5] might be adequate. However, the influence of such pre-conditioning on the initial properties of the samples is to be determined.

In this study, the pre-conditioning was used to investigate the behaviour of mortars with low expansion cements. In order to understand the changes induced by the pre-conditioning, the method of analysis developed by Massaad et al. [6] will be used to investigate experimental data as it allows evaluating the main phenomena of sulphate attack. Massaad's method is combined with a characterisation of the microstructure to assess the evolutions of both chemical and physical properties.

The pre-conditionning was originally designed for concrete samples with a drying temperature of 80 °C. For this study, it has been decided to apply the on the testing procedure developed by Massaad et al. [6] and involving mortar samples. The drying temperature has also been lowered considering that the sensitivity of the bearing-sulphate phases to temperature.

Four cements have been used in this experimental study: one sulphate resistant Portland cement with low-C_3A content (SR3), one sulphate resistant CEM III/B, and two blended slag-fly ash cements CEM V. The mortars were exposed to sodium sulphate in controlled conditions, with and without pre-conditioning. The temperature, concentration, and pH were kept constant [7]. External sulphate attack can be observed in different conditions with different pHs. In our study we focused on conditions with a pH of 7.5 (ground waters have a pH around 7.5 [8;9]). The macroscopic monitoring was based on length, mass, mass under water, and added acid volumes. First the materials and testing procedures are presented, including the method of analysis and the characterization of microstructure. Then the results are analysed and discussed.

2. State of the art

The concern for external sulphate attack made obvious the need of sulphate-resistant cements. There are two ways to specify if a cement is sulphate-resistant: it should have a good behaviour (no expansion, no cracking, no scaling) when exposed to a sulphate rich environment or its composition should meet specific requirements. Portland cements with a C_3A content limited to 5 % of the clinker are identified as sulphate-resistant (ASTM C 150 [10]). Nevertheless, these prescriptive specifications are pointless when it comes to new blended cements that overstep criteria. The implementation of performance test is expected to allow specifying the behaviour of new cements (Table 1).

Standard tests such as ASTM C 452 [11] describe the behaviour of mortars in which gypsum is added as a sulphate source. The restriction is a maximum expansion of 0.04% after 14 days. Although it is a quick test, its main constraint is that it can only be applied to Portland cement.

Table 1 External sulphate attacks: Existing test procedures

	ASTM C 452	ASTM C 1012	Maltais et al., 2004	Gruyaert et al., 2012	Leemann & Loser, 2012	Huang et al., 2015	Messad et al., 2010	El Hachem et al., 2012	Massaad et al., 2016	Lipus et al., 2018
Material	Mortar	Mortar	Paste	Concrete	Concrete	Mortar	Concrete	Mortar	Mortar	Mortar
Specimens	Prisms 25x25x285 mm^3	Prisms 25x25x285 mm^3	Discs of 15 to 20 mm thickness	Rotating dIscs	Cores of 28mm D 148mm L	-	Prisms 70x70x280 mm^3	Prims 20x20x160 mm^3	Cylinders of 20mm D 160mm L	Cylinders of 22mm D 160mm L
Pre-conditionniong	7 % SO3 mixed with mortar	None	None	None	Oven-drying at 50 °C for 120 ± 2 h, 5% Na2SO4 for 48 ± 2 h (4 times)	30V electrical field for 20 s alternatively with 20 s break	Oven-drying at 60°C until constant mass; 48h vacuum saturation	None	None	Water curing at 20°C 24 h then at 40°C for 9 days
Concentration (SO_4^{2-}, g/L)	-	33.8	0.96 and 4.8	3 and 30	33.8	33	6	3	3	3
Cation	Ca^{2+}	Na^+	Na^+	Na^+, Mg^{2+}	Na^+	Na^+	Na^+	Na^+	Na^+	Ca^{2+}, Na^+, Mg^{2+}
pH	Not controlled	6-8 after each measurement	< 10.5	Not controlled	Not controlled	Not controlled	Controlled at 7	Controlled at 7.5	Controlled at 7.5	Not controlled
Renewal of solution	/7 days then /28 days	1, 2, 3, 4, 8, 13, 15 weeks	/7 days	-	-	-	/4 weeks	/15 mL of added acid	/15 mL of added acid	-
Temperature	23+/-2°C	23+/-2°C	23°C	20°C	20°C	-	25°C	20°C	20°C	20°C, 5°C
Test duration	≥ 14 days	1 year	3 months	40 weeks	3 months	3 months	12 weeks	Not defined	Not defined	273 days
Monitoring	Length	- Length - Initial strength (> 20 MPa)	- XRD - SEM - EDX (Ca, S)	- Radius	- Length	- Sulphate concentration profiles	- Length - Porosity - Chloride diffusivity	- Length - Mass in air	- Length - Mass in air - Mass in water	- Length
Indicators	Expansion <0.04% after 14 days	Expansion <0.1% after 1 years	-	Radius variations	Expansion	-	Expansion, Pw, Dnssm	Expansion Mass	Expansion Mass Volume	Expansion <+0.07% at 273 days

Most of existing tests are based on expansion as the main indicator. A criterion of 0.1% expansion at 1 year [13] has been associated to ASTM C 1012 [12] test procedure. The main limitation of this test is its duration. Moreover, the use of expansion as the main indicator is also a restriction to apprehend the behaviour of cement if this results in little to no expansion during external sulphate attack. For instance, the qualification of the blended CEM V cements as sulphate-resisting cements is undermined by the expansion criteria. On site, CEM V cements have generally shown a good behaviour in sulphate-rich environments. In laboratory conditions, significant expansion of sulphate-resistant materials could not be observed in short testing times. New indicators are needed to assess the degradation in the absence of expansion. In the meantime, tests have been designed to shorten the response time (that is the time when expansion becomes noticeable) thus they are worth to be considered in this study.

There are different ways to accelerate a sulphate resistance test. Conditions can be chosen in order to get a response time as short as possible. Drying and immersion cycles [14, 15] are often used to accelerate the degradation. However, this type of test is often coupled with a high concentration in sulphates. Thermal pre-conditioning can also be coupled with saturation to create a concentration gradient which allows the sulphates to penetrate the material before diffusion. Leeman and Loser [16] proposed a revised version of an accelerated standard test (SIA 262/1:2013 [17]), 3 months being an ideal time.

Sulphates diffusion through the material can also be stimulated by electrical pulsations [18]. Sulphates penetrate the material by migrating from the cathode to the anode. The concentration gradient also allows the sulphates to diffuse from the cathode to the anode. Immersion tests were also performed to confirm the acceleration. The sulphate concentration profiles after 3 months showed that the sulphate penetration within the material was accelerated. Nevertheless, this testing procedure influenced the external sulphate attack mechanism. No brucite was found in the samples in contact with magnesium sulphate solution while this hydrate is distinctive of this kind of sulphate attack [19].

Messad et al. [20] also proposed a procedure for testing concrete. The specimens are oven-dried at 80°C until constant mass, then saturated with a sodium sulphate solution at 8.9 g/L under vacuum. After this pre-conditioning stage, the samples were immerged in a sodium sulphate solution (8.9 g/L) with pH controlled at 7. The concrete samples made with non-sulphate resistant cements, generally showed significant degradation after 12 weeks, implying that the degradation process had been accelerated. This pre-conditioning is very convenient and easy to implement. Since it is set on the samples it can be combined with various testing procedures, allowing to apply representative testing parameters. However, the drying process is likely to modify the microstructure of the samples and thus the sulphate attack mechanism. Messad et al. [5] addressed this question by measuring the sulphate diffusion coefficients. The evolution of the coefficient all along the test was in accordance with the known degradation mechanism. However, the drying temperature rises question. However, the drying temperature rises question. Many hydration products are overly sensitive to temperature. The stability of ettringite differs greatly depending on the pressure and temperature conditions. It is acknowledged that ettringite will decompose at 80°C.

High sulphate concentrations of the order of 30 g/L have been used in some previously described test procedures. Increasing sulphate concentration is known to accelerate the expansion-inducing phenomena [21] but it is not representative of most of field conditions. The performance test designed at GeM Laboratory allows controlling the exposure conditions accurately thus investigating several testing parameters. Mortars specimens [7] were preferred over concrete [22]. The choice of the material has a great impact on the duration of the test. Since the diffusion of sulphate is the limiting step, using smaller samples shortens the sulphate penetration time.

The test developed at GeM Laboratory allows a control of exposure conditions [21; 6]. Controlled pH allows to maintain favorable conditions for the reaction. In a close environment, such as our testing device, the pH of the sulfate solution would quickly increase to around 12-13 because of the buffer effect of portlandite leaching. Once the pH is stable around 12-13 there is no more porlandite leaching. It has been demonstrated that there is a strong correlation between portlandite leaching and external sulphate attack [23]. Samples expand more at pH=7 than pH=12 [24]. The application of the performance-based strategy [25] gives valuable information on the progress of degradation, such as the macroscopic volume variation and the microscopic volume variations associated to the main phenomena involved in external sulphate attack. Moreover, this strategy makes possible the evaluation of the behaviour of sulphate-resisting cements with low expansion. In the meantime, these experimental and analytical tools allow investigating the influence of the thermal pre-conditioning on the sulphate attack mechanism.

3. Materials and methods

In order to understand the influence of the thermal pre-conditioning, two sets of specimens have been prepared and two testing procedures have been implemented. Two CEM V cements were compared with two sulphate resistant cements.

3.1 Materials and samples preparation

The tested CEM V cements were of CEM V/A 32.5 N and a CEM V/A 42.5 N types, named respectively CEM V1 and CEM V2 (Table 2). They contain fly ash (19%) and slag (22%). The other cements were a Portland cement CEM I 52.5N, noted SR3, according to EN 197-1 (Table2) and a CEM III/B. The compositions of the cements are displayed in Table 2. The mineralogical composition and especially the C_3A content is obtained by Bogue calculation derived from the clinker chemical composition (% wt oxides). However, XRD analysis allowed detecting a small amount of aluminates.

The mortar mixtures were derived from standard mortar composition [26] keeping the volume of sand and cement paste constant. In order to facilitate the penetration of sulphate a water- to-cement ratio (w/c) of 0.6 was chosen. French standard sand (SNL, 0.08 mm – 1.6 mm size) is used to produce mortars according to the standard EN 196-1. This is natural siliceous sand with generally isometric and rounded particles shape [27].

Table 2 Mineralogical (XRD) composition of clinkers and chemical (XRF) composition of cement (producer's data)

		Method	SR3	CEM III	CEM V1	CEM V2
Mineralogical composition of clinker (%)	Alite	DRX	66,9	53.8	64.4	61,9
	Belite	DRX	7,9	11.5	11.1	20.2
	Aluminates	DRX	0,9	7.7	11.1	3.9
	Ferrites	DRX	19,7	3.8	4.4	12.5
	Periclase	DRX	2,6			
Amorphous phase (%)	[Slag+Fly ash]	DRX	-	74	49	44
Sulphated additions	Anhydrite	DRX	1.7	-	2	-
	Gypsum		-	3	<1	1.7
Chemical composition of cement	L.o.I. (950°C)	SFX	0,09	2,44	1,86	0,31
	SiO_2	SFX	20,50	28,8	30,4	31,13
	Al_2O_3	SFX	3,69	8,53	10,21	9,99
	Fe_2O_3	SFX	6,88	1,47	3,05	3,91
	CaO	SFX	63,5	47,6	46,00	45,9
	MgO	SFX	3,58	5,4	2,57	2,59
	SO_3	SFX	0,72	3,12	2,67	2,92
	K_2O	SFX	0,61	0,49	1,1	1,96
	Na_2O	SFX	0,34	0,22	0,24	0,40
	SrO	SFX		0,11	0,13	0,03
	TiO_2	SFX		0,54	0,55	0,27
	P_2O_5	SFX		0,1	0,23	0,43
	MnO	SFX		0,17	0,15	0,06
	Sum		**99,91**	**98,99**	**99,16**	**99,90**

For each cement and testing procedure, the mortar mixture was prepared according to the standard NF EN 196-1[26]. The samples were 160 mm long and 20 mm diameter cylinders. They were stored in a moist room at 95% relative humidity until their compressive strength reached 20 MPa. Then, the samples were placed in saturated limewater for 28 days. Control samples were also made and later kept in tap water to distinguish the effects of hydration and sulphate attack.

3.2. Testing procedures

Both testing procedures consist in exposing mortar samples to sulphate in saturated conditions and monitor their evolution. The first testing procedure consists in immersing mortar specimens in a sodium sulphate solution directly after water curing; the second testing procedure includes a thermal pre-conditioning stage.

3.2.1. Thermal pre-conditioning procedure

Two samples of the second batch were pre-conditioned according to a modified version of the methodology developed by Messad et al. [5]. The samples were dried in an oven at a temperature of 60°C. The drying process was considered complete when the mass variation during 24h did not exceed 0.1%. It took approximately 1 week, followed by the saturation stage. The samples were put in a vacuum desiccator for 4 hours, then a sulphate solution was added, the vacuum still being on. A sodium sulphate solution with a concentration of 4.44 g/L, that is 3 g/L of sulphate, was used. The samples were saturated with the sulphate solution for 44 hours. Fig. 1 represents the main stages of the testing procedure for both samples with and without pre-conditioning.

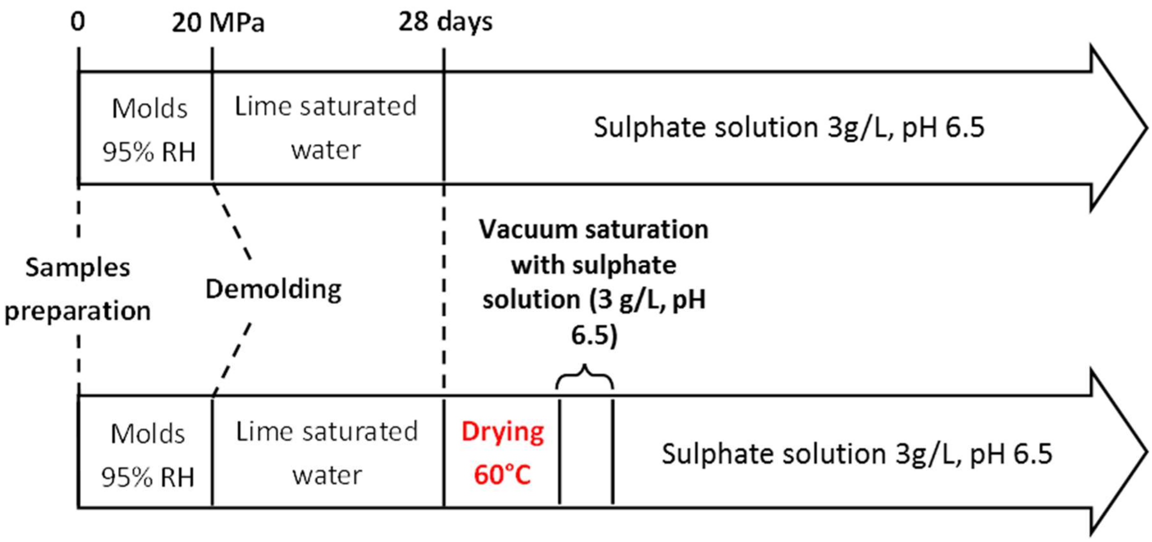


Fig. 1 Process of testing procedure without pre-conditioning (top) and with pre-conditioning (bottom)

3.2.2. Conditions of sulphate exposure

For each cement and testing procedure (with and without thermal pre-conditioning), two specimens were immerged in a sodium sulphate solution with a sulphate concentration of 3g/L (Fig. 2). The solution was prepared in the same way as the saturation solution. The temperature was kept at 20°C with a cooling system and water circulation in double walled beakers. To keep the pH constant at 7.5, 0.5M nitric acid was automatically added by burettes and the cumulated volume of added acid was monitored. The sulphate solution was renewed as soon as 15 mL of nitric acid were added. During the renewals, the measures of monitored parameters were performed.

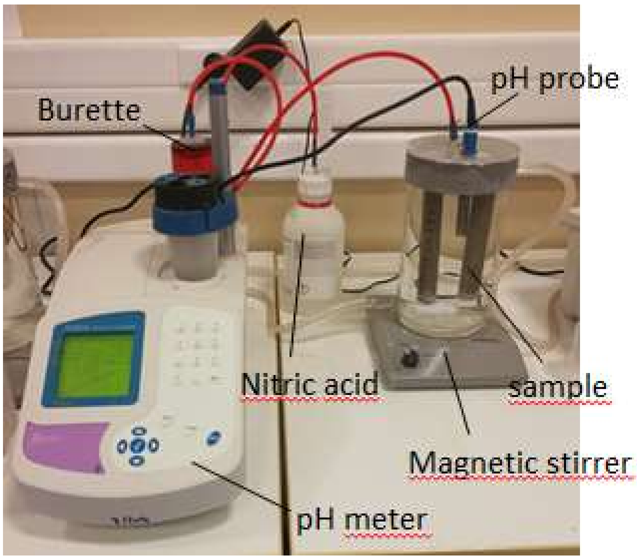


Fig. 2 Mortar samples in cell containing sulphate solution

3.2.3. Monitoring measurements

The samples were first weighed under water in a container filled with the same sodium sulphate solution. Then their surfaces were carefully dried with a paper towel and their mass was measured. The length variations were determined by comparison with a reference invar bar on a comparator Mitutoy Absolute ID-5112XB with a resolution of 0.001 mm. Mass under water, mass and length variations of control samples were measured at the same time. The first measurement was performed just before the samples were introduced in the cell, that is after 28 days in lime saturated water for the samples without pre-conditioning and after the vacuum saturation phase for the samples with pre-conditioning.

3.3. Characterisation of microstructure

3.3.1. Thermogravimetric analysis (TGA)

The portlandite and sulphate content of the samples were determined by thermogravimetric analysis (TGA). After being powdered and sieved at 0.160mm, a small part of the sample was placed in an alumina crucible. The analyses were performed using a NETZSCH® STA 449F3 system. The samples were heated at 10 °C/min from 25 °C to 1400 °C under an inert atmosphere of nitrogen.

3.3.2. Mercury intrusion porosimetry (MIP)

Cylindrical mortar samples of 1.5 cm height were sawn from sound samples after they have been kept 28 days in water, after drying at 60 °C and after saturation in sulphate solution. Measurements were performed on Micromeritics AUTOPORE IV 9500 porosimeter. The range of pore diameter was from 3 nm to 1 mm. The mercury intrusion curves were analyzed to determine the pore size distribution, the porosity, and the median pore diameter.

3.3.3. X-ray diffraction (XRD)

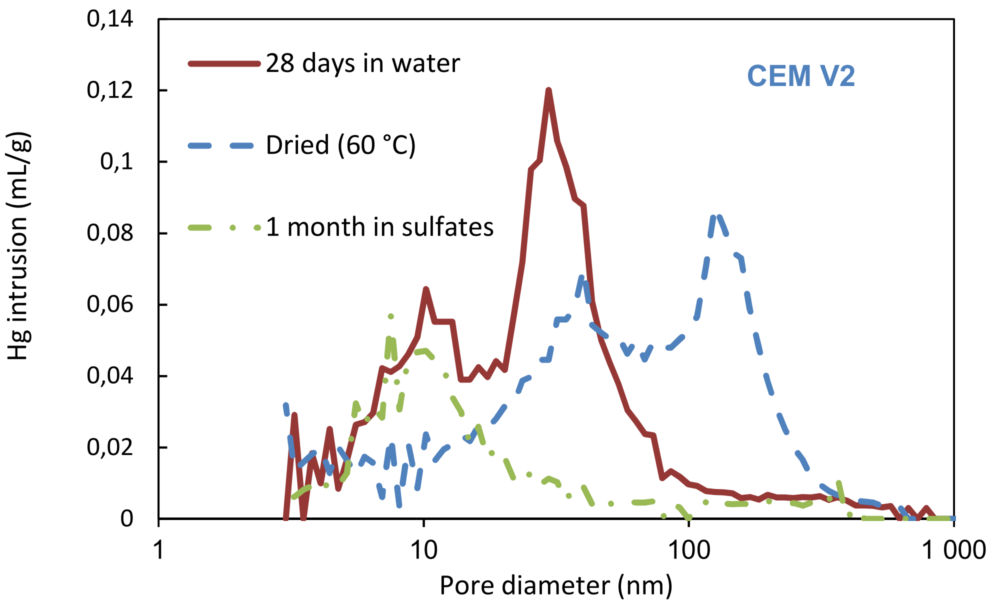
Cylindrical specimens sawn from control and tested samples were first grinded. Then their X-ray diffractograms have been collected on a Bruker D4 device with a θ-2θ configuration and CuKα radiation ($\lambda_{CuK\alpha}$ = 1.54 Å) at 40 KV and 40 mA. The samples were analyzed at a 2θ rotation step of 0.02° and a rotation speed of 0.5 s/step over a total angle of 70°.

4. Results and discussion

4.1. Initial microstructure and sulphate exposure conditions

To understand the influence of the pre-conditioning on the degradation mechanism it is important to characterize its effect on the microstructure of the samples. SR3 and CEM V2 samples have been characterized at different stages of the pre-conditioning and testing procedure, in order to grasp the influence of the pre-conditioning on a SR cement and on a CEM V cement. XRD, TGA and mercury intrusion porosimetry (MIP) have been carried out on the samples after 28 days at the end of curing in lime saturated water. The same characterization steps have been performed on samples after the drying process at 60°C. Finally, the samples have been characterized after the saturation phase and one month in sulphate solution.

The characterization of samples with MIP is displayed in Fig. 3. After 28 days in water SR3 samples had a porosity of 14.1% with an average pore diameter of 35nm. CEM V2 had a porosity of 16.8 % and an average pore diameter of 30nm (Table 3). After the drying process both samples saw their porosity increase. This is a result of the dehydration and the apparition of microcracks within the sample [28]. Dried SR3 sample had a porosity of 19.4 % and an average pore diameter of 93nm. The values for dried CEM V2 are slightly lower with a porosity of 17.4% and an average pore diameter of 72.8nm. While the samples seemed to react the same to the drying process, the results observed after the saturation phase are different. Saturated SR3 sample exhibit a porosity and an average pore size quite similar to the ones after 28 days in water, but still higher: 17.8% and 41nm. CEM V2 saturated samples, on the other hand, had a lower and finer porosity. With an average pore diameter of 23nm and a porosity of 9.9%, CEM V2 samples with pre-conditioning have a pore structure that is significantly different from the samples without pre-conditioning.



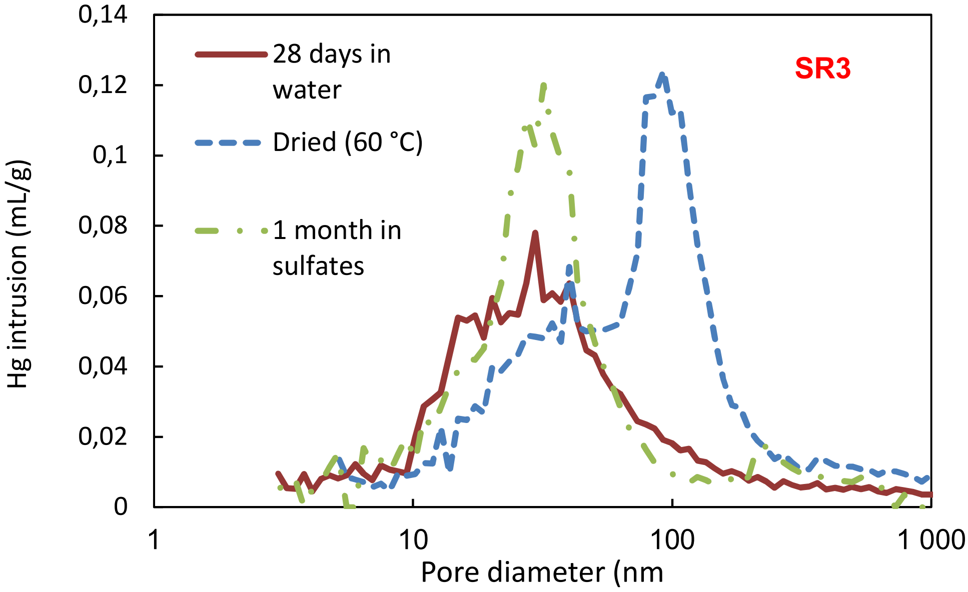


Fig. 3 Pore size distributions of CEM V2 and SR3 samples from MIP

Drying process affected the pore structure of both SR3 and CEM V2 samples. Saturation and hydration in sulphate only partly compensated the effect of drying on SR3. Concerning CEM V2, the observed microstructural changes are characteristic of higher hydration degree [29]. The hydration of binders with fly ash and slag depends on several parameters such as particle size distribution and amorphous content, but it is generally slower than plain Portland cement. Thus, the acceleration of their reactivity has been widely studied. High temperature, sulphates, and relatively high pH have already been shown to foster their reactivity [30].

Pre-conditioning also resulted in lower portlandite content (Table 3). The precipitation of sulphate-rich phases has been found to be strongly correlated with portlandite dissolution [31]. Thus, the influence of pre-conditioning could be partly due to its effects on the composition of hydrated cement paste. XRD did not allow concluding on significant differences between SR3 and SR3 PC samples, as the accuracy of the analyses was affected by remaining crushed sand particles. Ettringite nearly disappeared after 60 °C drying then formed again after immersion (Appendix A). The influence of temperature on the stability of ettringite and monosulfoaluminate is well known [32]. The influence of pre-conditioning on porosity and pore size diameter could also be due to the effects of high temperature and drying on the nanostructure of CSH.

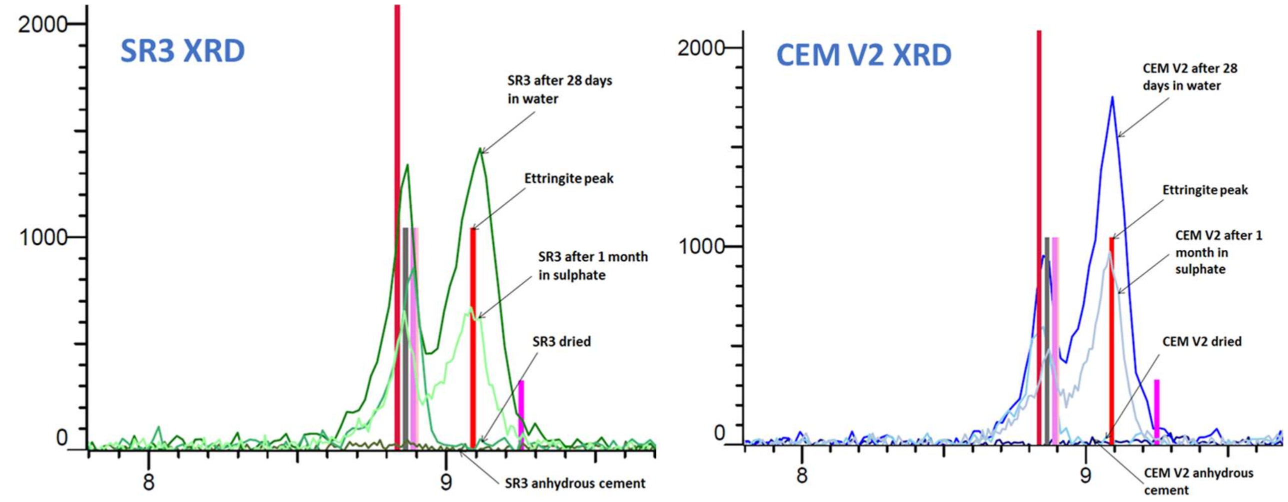


Fig. 4 Close up ettringite peak on XRD diffractograms

The close up on the ettringite main peak (fig. 4) shows that it has disappeared after drying for SR3 and CEM V2. The peak is also smaller for both cements after saturation.

Globally, the peak intensities are different after 28 days in water, drying and saturation, but it is difficult to conclude because of the presence of amorphous phases. Moreover, the peak intensities also depend on the crystallization. TGA confirmed that there was less portlandite after drying and saturation (table 3).

Table 3: Results of MIP and TGA analyses of SR3 and CEM V2 samples

	28-day water curing	60°C oven-drying	1-month sulphate exposure
SR3			
Median pore diameter (nm)	35.3	92.6	40.6
Porosity (%)	14.1	19.4	17.8
Portlandite, $Ca(OH)_2$ (%)	27.4	nd	14.7
CEM V2			
Median pore diameter (nm)	30.4	72.8	23.3
Porosity (%)	16.8	17.4	9.9
Portlandite, $Ca(OH)_2$ (%)	10.8	nd	4.0

Pozzolanic cements are recommended to mitigate delayed ettringite formation (DEF) [33]. DEF occurs when high temperature in concrete at early-age prevents the formation of ettringite. This appears later in hardened concrete, causing crystallisation pressure and extensive cracking. High temperature and alkaline environment result in faster hydration of pozzolanic cements, and maximum temperature is mitigated due to lower total clinker content. Pozzolanic reactions produces denser C(A)SH with lower pore diameters. This allows reaching lower diffusivities thus mitigating the ingress of chloride and sulphate ions, but smaller pores are likely to induce higher crystallisation pressure. However, this effect seems to be compensated by slower micro-diffusion of sulphate ions through hydrated cement paste and lower availability of aluminates. CEM V samples were exposed to sulphate solution after 28 days. The hydration of the clinker part was likely significant thus aluminates were available to react with sulphates ions and produce ettringite. In CEM V PC samples, aluminates can be assumed to be less available due to partial embedment in CASH phase and less accessible due to finer porosity.

4.2 Direct monitoring indicator

The pre-conditioning had a direct influence on the initial microstructure of the SR0 and CEM V2 samples. The monitoring of mortar specimens exposed to sulphate solution according to both testing procedures allowed quantifying the influence of initial microstructure and exposure conditions on the degradation mechanism.

The main consequence of external sulphate attack is the formation of new phases, causing expansion and cracking [34]. Therefore, the most common indicator used to assess the degradation of samples during tests is expansion. Fig. 5 represents the length variation of the mortar specimens without pre-conditioning that will be simply designated with the name of the cement. The specimens with pre-conditioning will be distinguished with PC acronym. The horizontal and vertical bars on the Fig. 3 and 4 indicate the criteria mentioned by Lipus et al. [35]; i.e. maximum expansion of 0.08 % after 9 months. The length variations are defined as the relative difference between current value of length and initial value:

$$(L(t) - L0)/L0 \quad (1)$$

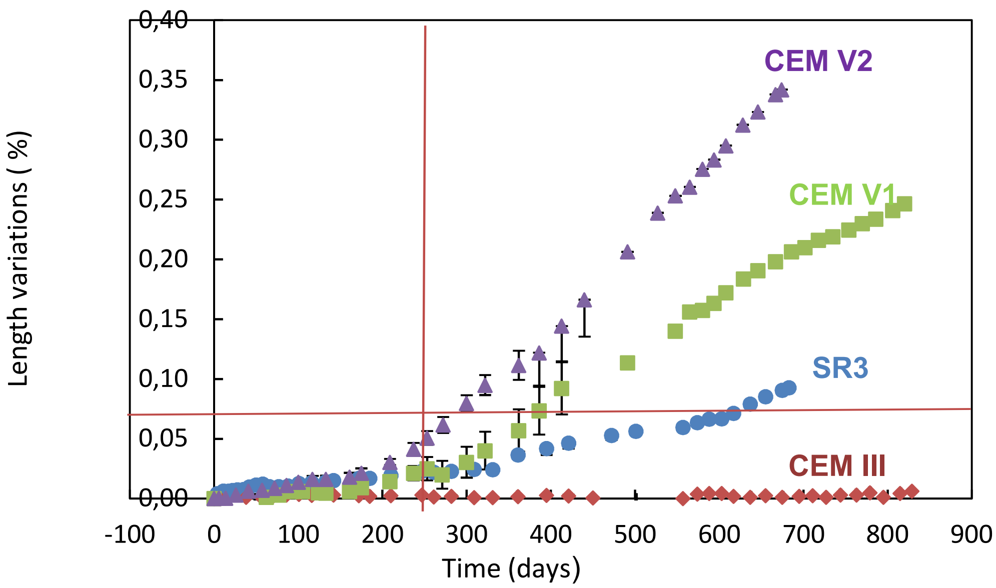


Fig. 5 Length variation of specimens without pre-conditioning

After more than 800 days, CEM III showed no expansion (fig. 5). Among the tested cements, CEM V2 samples went through the highest expansion. Their length increased by 0.34% after 674 days. They also started swelling first. The other CEM V cement sample, CEM V1, reached 0.25 % after 820 days, then come SR3 samples with 0.09% after 683 days. The length variations of the samples CEM V and SR3 might seem relatively high but they meet the criteria of sulphate-resisting cement. SR3 and the two CEM V started expanding after 200 days with a relatively low rate. Their expansion did not exceed the criteria mentioned by Lipus et al. [29].

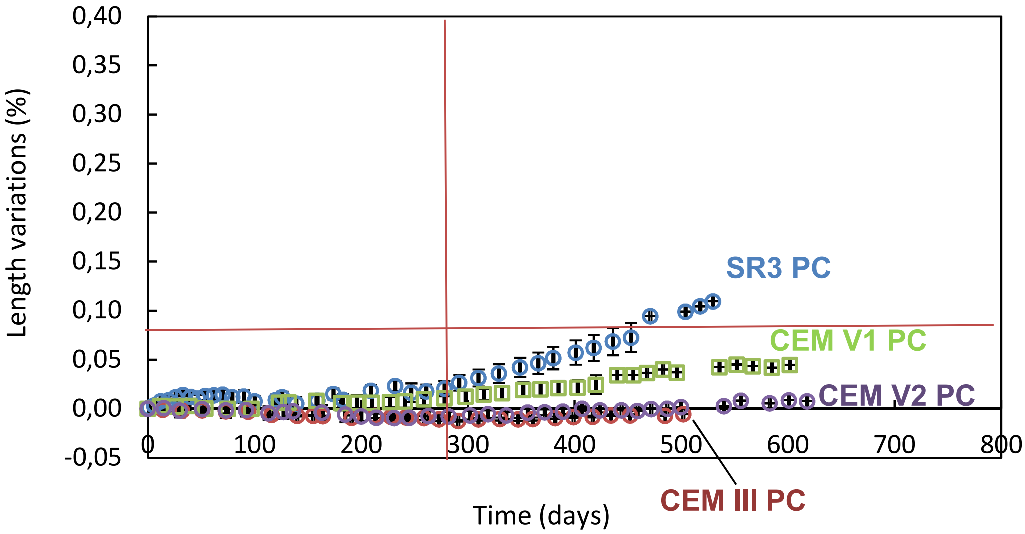


Fig. 6 Length variations of specimens with pre-conditioning

Fig. 6 displays the length variations of the samples with pre-conditioning. As for the samples without pre-conditioning, expansion began after 200 days. SR3 samples showed the highest expansion of 0.11%. CEM V1 is the only other expanding mortar with a maximal value of 0.04%. The pre-conditioned CEM III sample did not show any expansion just as the sample without pre-conditioning. CEM V2 PC also showed no expansion, unlike CEM V2. The thermal pre-conditioning clearly changed the ranking of the studied materials. The expansion of SR3 PC was higher, which implies an acceleration of the degradation process, whereas the expansion of CEM V samples decreased, especially for CEM V2 now showing lower expansion than CEM V1.

The behaviour of SR3 samples can be interpreted by referring to Messad's results [4]. Sulphate attack first induced a decrease of sulphate diffusivity then it significantly increased. This could explain why the effect of pre-conditioning only appeared after more than 270 days approximately. The behaviour of CEM V samples was totally different. The finer porosity of CEM V2 PC slows down the penetration of sulphate within the samples and thus modifies the degradation process.

As useful as it is, this indicator does not give much more information on the degradation process. More data are needed to understand more deeply the influence of the thermal pre-conditioning on the mechanism of degradation. In this perspective, the mass variations of the samples with and without pre-conditioning are presented in Fig. 7.

Only SR3 PC mass loss was higher than SR3 mass loss from the beginning. There was a quasi-linear correlation between both sets of data for the whole testing time. For CEM V PC, mass losses were slightly lower than the CEM V mass losses during the first stage. It changed after 200 days. At this time, the length of CEM V samples started to increase, meaning that expansive compounds were formed. These new phases partly compensated the mass losses. As CEM V2 PC did not show any expansion and CEM V1 PC a much lower expansion than CEM V1, their higher mass loss could indicate a lower precipitation of new phases. The case of CEM III and CEM III PC is different as the two samples did not expand, but still CEM III PC mass loss overtook CEM III mass loss after 400 days. Before this point, the mass loss was higher for CEM III.

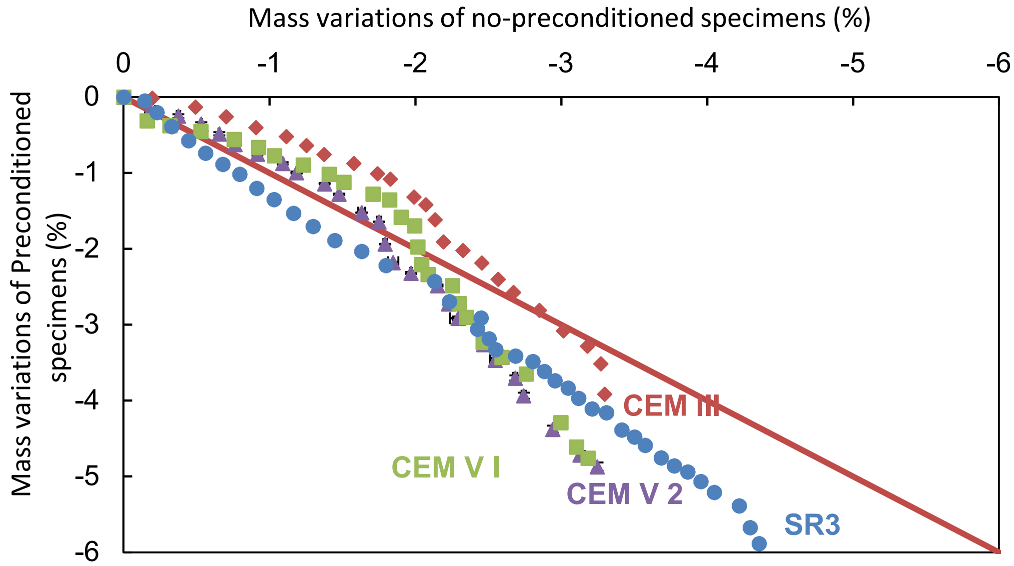


Fig. 7 Mass variations of PC samples in regard to mass variations of samples without pre-conditioning. The red line corresponds to slope=-1.

The mass changes of studied materials result from several phenomena, such as dissolutions and precipitations, loss of solid particles such as aggregates, and cracking. A continuous mass loss indicates that leaching and aggregates loss prevailed. Leaching was assessed from cumulated volumes of added acid. The leached OH^- is shown in Fig. 8.

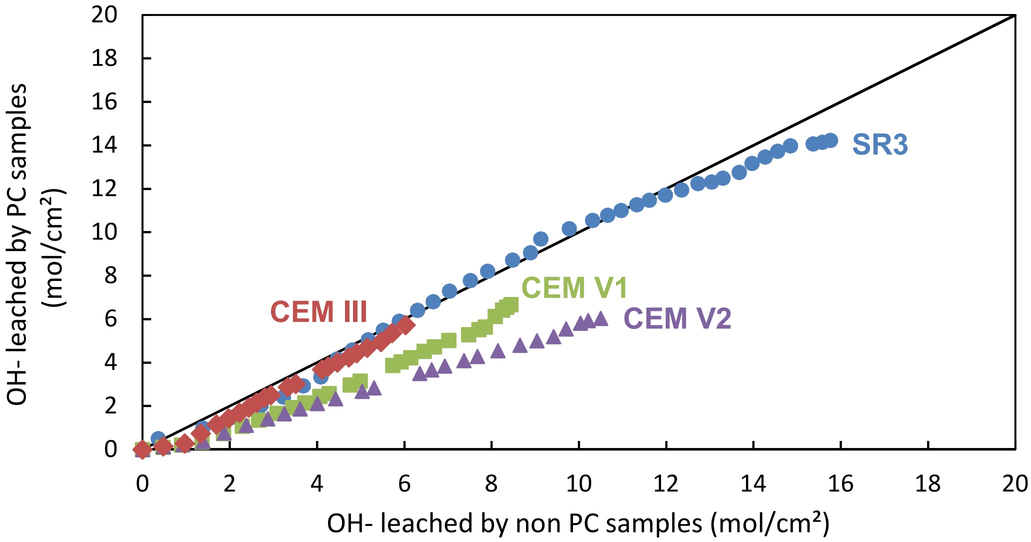


Fig. 8 Leached hydroxides ions of PC samples with regard to leached hydroxides ions of samples without pre-conditioning

SR3 PC and CEM III PC had the same amount of hydroxide ions leached as their no preconditioned samples. As expected, SR3 had the highest leaching of hydroxide ions. CEM III showed the lowest leaching magnitude, but the mass variation curves (Fig. 7) showed that CEM III mass loss was identical if not higher than the CEM V ones. Higher mass loss in CEM III samples associated to lower leaching could thus correspond to lower amounts of precipitation, which would be consistent with negligible expansion, unlike CEM V samples. The CEM V curves were similar until 200 days, meaning that the two CEM V cements (with and without pre-conditioning) had the same leaching kinetics. Then the ratio of leached hydroxide was higher for CEM V1 than CEM V2 but both were lower than 1 (Fig. 8). CEM V PC lost less hydroxide ions. This seems consistent with previous results. During the first stage, their mass loss was actually lower (Fig. 7). The degradation of CEM V samples was slowed down by pre-conditioning, as indicated by expansion and mass loss data (Fig. 6 and 7). This was clearer for CEM V2 PC samples than for CEM V1, and CEM V2 showed the most significant decrease in leaching kinetics (Fig. 8). It is congruent with the lowest portlandite content measured in CEM V2 samples after drying and saturation (table 3).

All the samples lost mass, even the ones with minor expansion. The mass indicator corresponds to the mass of saturated specimens with surface dried (SSD), thus the volume includes the cracks and open porosity filled with water. This does not allow concluding on the influence of precipitations, dissolutions, and aggregates loss on the volume of solid phase. Combining the SSD mass with the measurement of the mass under water (1) allows determining the volume variations of solid phases (Fig. 9).

$$\Delta V = \frac{\Delta m - \Delta m_{sol}}{\rho_{sol}} \quad (2)$$

Where:

Δm is the variation of the mass at SSD state in air, Δm_{sol} is the variation of the mass in sulphate solution

ρ_{sol} is the density of the sulphate solution

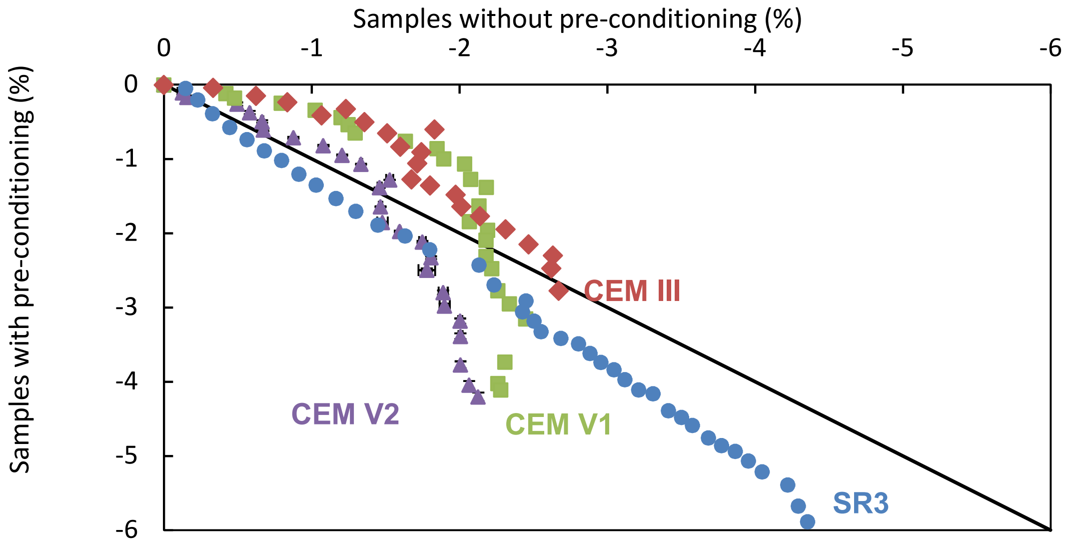


Fig. 9 Volume variation of PC samples with regard to volume variations of samples without pre-conditioning

The volume variation of the samples with pre-conditioning had the same tendencies as their mass variations. SR3 PC had a greater volume decrease than SR3. The two CEM V PC volume decrease overstepped the CEM V volume decrease around 300 days. A higher volume decrease of CEM V PC means that lower amounts of precipitated phases was formed. As the formation of new phases is likely to cause crystallisation pressures, this result is consistent with lower expansion of CEM V PC specimens.

From these results, thermal pre-conditioning did accelerate SR3 degradation. This might be due to the slightly higher porosity of SR3 PC samples (table 3). However, the acceleration was mild, SR3 PC had greater length variations than SR3 but both samples started swelling at the same point (Fig. 4 and 5). As for the CEM III and CEM V samples, the thermal pre-conditioning brought no acceleration. It even slowed down the expansion of the CEM V samples and changed the whole degradation process since expansion could not compensate the loss of material in surface affecting mass measurements. The destruction of ettringite by drying and its reformation after saturation led to a finer porosity that slowed down the penetration of sulphates and, consequently slowed down the expansion phase.

The strategy developed by Massaad et al. [6] was applied to determine if the pre-conditioning not only affected the initial microstructure of the samples but also the products formed during the external sulphate attack. Part of this strategy allows the determination of the main precipitated and main leached hydrates during the external sulphate attack.
The densities of leached and formed phases in samples with and without pre-conditioning are compared in Fig. 10. Both graphs confirm that pre-conditioning had a minor influence on the leached and precipitated phases. The density (Fig. 10) indicates that leached phase was mainly portlandite. The density of the sulphate-rich phase lies between ettringite and gypsum. The values are the same for samples with and without pre-conditionning. It implies that the differences observed in the degradation process of the samples, especially the CEM V samples, are not caused by different chemical reactions.

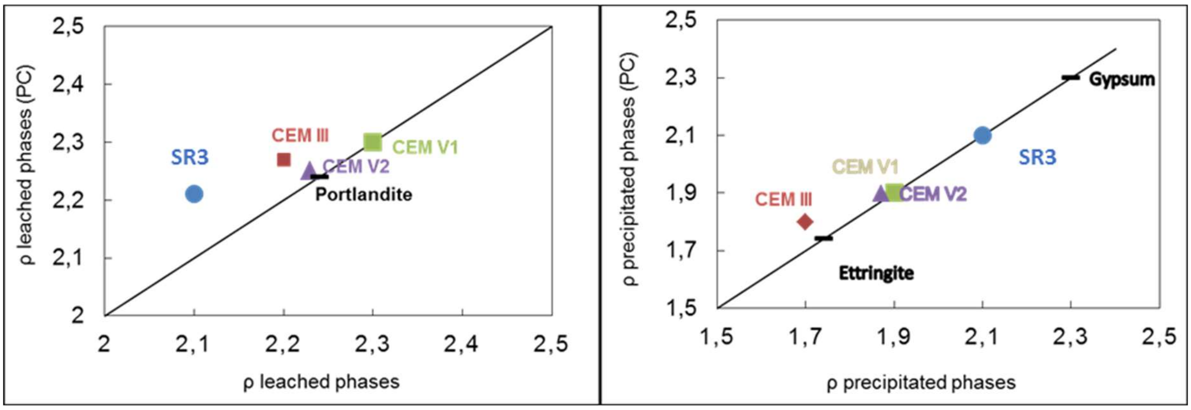


Fig. 10 Densities of leached (left) and precipitated (right) phases

5. Conclusion

Two sulphate-resisting cements, a SR3 Portland cement, and a CEM III/B slag cement, as well as two blended slag-fly ash cements CEM V were subjected to laboratory external sulphate attack. In order to study the effect of a pre-conditioning, involving a heat treatment and a saturation phase, aimed at shortening the response time to external sulphate attack, the behaviour of samples with and without pre-conditioning was analysed. The following conclusions can be drawn.

- The initial microstructure was strongly modified by pre-conditioning with different trends depending on cement composition. The pre-conditioning resulted in lower and finer porosity of CEM V mortars.
- The thermal pre-conditioning was originally designed to accelerate the expansion of concrete samples and distinguish their behaviour in sulphate rich environment (from sulphate-resisting ones). The implementation of this procedure gave low expansion on small mortar samples. In our testing conditions, the oven drying and vacuum saturation did not result in a significant acceleration of the degradation process, and in some cases, it mitigated the consequences of

sulphate attack, thus the ranking and the qualification of studied materials in terms of sulphate resistance changed. While CEM V samples with pre- conditioning showed a very weak expansion, CEM V without pre- conditioning exhibit some expansion of a magnitude close to CEM I SR3

- We assume that pre- conditioning does not affect degradation mechanism at the chemical level, while the microstructure is strongly modified by pre-conditioning, inducing different trends depending on cement composition. The pre-conditioning resulted in lower and finer porosity of CEM V mortars.
- The thermal pre-conditioning allowed a slight acceleration of the degradation process of SR3 samples. However, the effect of the pre-conditioning is limited by the composition of the cement. Unlike CEM V samples, SR3 samples responded positively to the sulphate saturation phase. Still the residual expansion of SR3 PC samples began at the same time as SR3 samples. De facto, SR3 clinker composition was too poor in aluminate to react with sulphates. The same observation can be made for CEM III samples. CEM III mortar with and without preconditioning did not expand, even after a significant exposure time to sulphates.
- The thermal pre-conditioning cut out the phase of sulphate penetration. However, this diffusion stage is characteristic of external sulphate attack. The way a given cement-based material can cope with this phenomenon should also be a part of the sulphate resistance of the cement.
- The monitoring allowed characterizing the main phenomena involved in sulphate attack. From the properties of leached and precipitated products, we can assume that the degradation mechanism was not affected at the chemical level,
- The test as itself, without pre-conditioning, is applicable for low-expansion cement and shows exploitable results, helpful to understand the behavior of CEM V cements to external sulphate attack.

Appendix A. XRD analyses of tested mortars

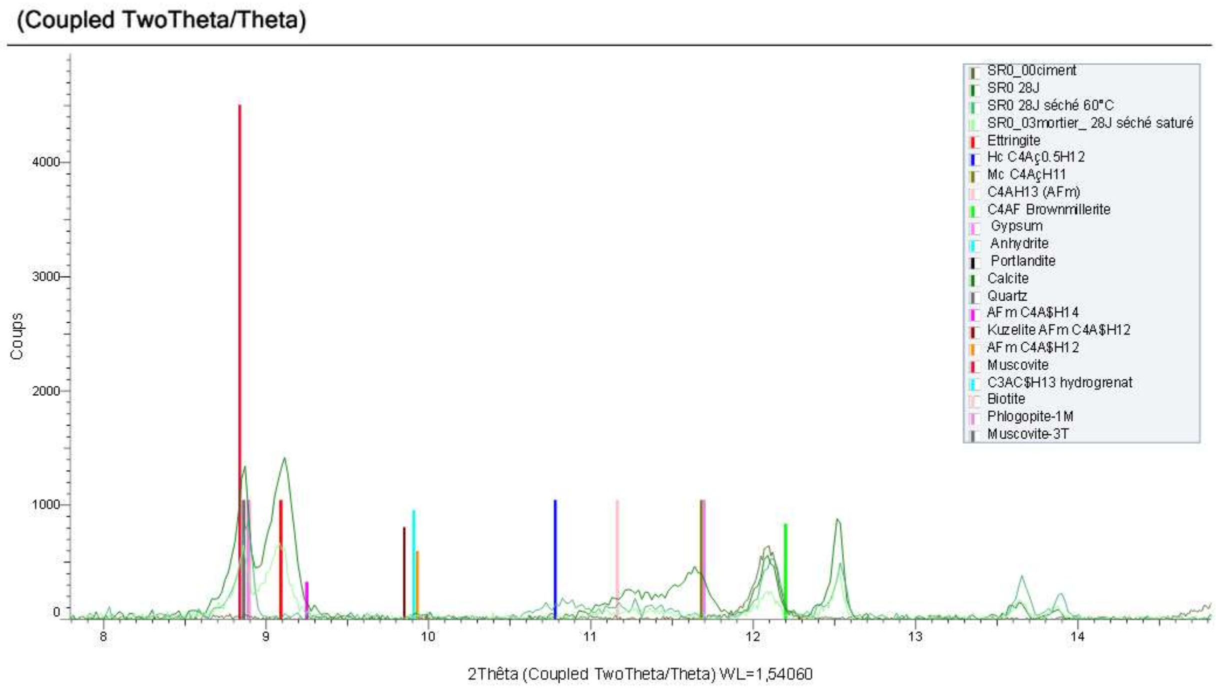


Fig. A.1. XRD analyses of SR3 mortar samples before and after pre-conditioning and after 1-month immersion.

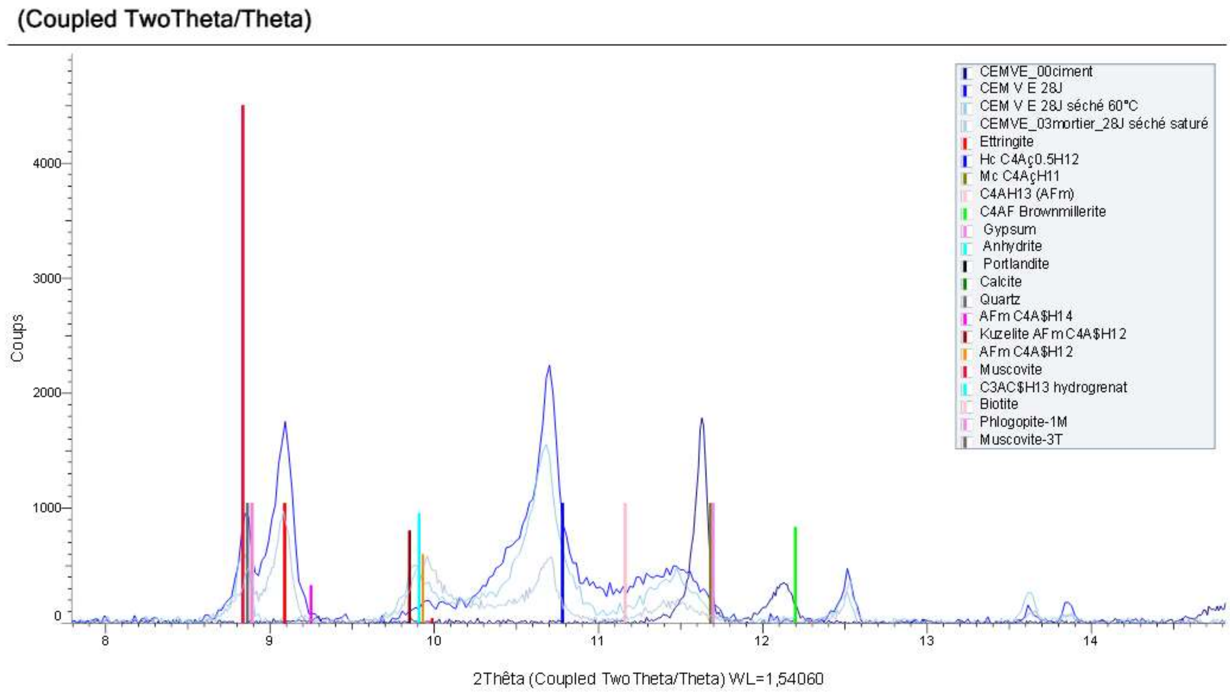


Fig. A.2. XRD analyses of CEM V2 mortar samples before and after pre-conditioning and after 1-month immersion.

Acknowledgements The cement producers are also gratefully acknowledged for providing the cement samples and their analysis. The authors would also like to thank Laetitia Bessette (Vicat at L'Isle D'Abeau, France) for performing the XRD analyses on mortar and fruitful discussions.

Author contributions Conceptualization, S.B., A.L., E.R.; Validation, S.B., A.L., E.R., L.I.; Investigation S.B., A.L., E.R., L.I.; Writing-original draft, S.B.; Writing-review and editing A.L., E.R., L.I.

Availability of data The data that support the findings of this study are available from the corresponding author, A. L., upon reasonable request.

Funding The authors would like to thank French National Agency for Technological Research (ANRT), ATILH (Paris, France), and Ecole Centrale de Nantes (Nantes, France) for their financial contribution support.

Compliance with ethical standards

Conflicts of interest The authors declare no conflict of interest

References

1. Neville, A., 2004. The confused world of sulfate attack on concrete. Cement and Concrete Research 34, 1275–1296.
2. Collepardi M., 2003. A state-of-the-art review on delayed ettringite attack on concrete, Cement and Concrete Composites 25, 401-407.
3. Ping, X., Beaudoin, J.J., 1992. Mechanism of sulphate expansion I. Thermodynamic principle of crystallization pressure. Cement and Concrete Research 22, 631–640.
4. Scherer, G. W., 2004. Stress from crystallization of salt. Cement and Concrete Research 34, 1613-1324.
5. Messad, S. Mise au point d'un essai de vieillissement accéléré à l'attaque sulfatique externe pour l'application du concept de performance équivalente dans le cadre de la norme NF EN 206-1, PhD Thesis, université de Toulouse III – Paul Sabatier (2009)
6. Massaad, G., Rozière, E., Loukili, A., Izoret, L., 2016. Advanced testing and performance specifications for the cementitious materials under external sulfate attacks. Construction and Building Materials 127, 918–931.
7. El Hachem, R., Rozière, E., Grondin, F., Loukili, A., 2012. New procedure to investigate external sulfate attack on cementitious materials, Cement and Concrete Composites 34, 357-364.
8. Leemann, A., Loser, R., 2011. Analysis of concrete in a vertical ventilation shaft exposed to sulfate-containing ground water for 45 years. Cement and Concrete Composites 33, 74-83.
9. Vencelides, Z., Hrkal, Z., Prchalova, H., 2010. Determination of the natural background content of metal in ground waters of the Czech Republic. Applied geochemistry 25, 755-762.
10. ASTM C 150 – 04a, Standard specification for Portland cement, ASTM, 2002
11. ASTM C 452 – 19e1, Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate, ASTM
12. ASTM C 1012 - Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution
13. Gonzalez, M.A., Irassar, E.F., 1998. Effect of limestone filler on the sulfate resistance of low-C_3A Portland cement, Cement and Concrete Research 28, 1655-1667.
14. Maltais Y, Samson E., Marchand J., 2004. Predicting the durability of Portland cement systems in aggressive environments – laboratory validation, Cement and Concrete Research 34, 1579-1589.
15. Gruyaert E., Van den Heede P., Maes M., De Belie N., 2012. Investigation of the influence of the blast-furnace slag on the resistance of concrete against acid or sulphate attack, Cement and Concrete Research 42, 173-185.

16. Leemann, A., Loser, R. Accelerated sulfate resistance test for concrete – chemical and microstructural aspects, Second international conference on microstructural – related durability of cementious composites, 2012, Amsterdam
17. SIA 262/1:2013, 'Annexe D – Résistance aux sulfates', pp 27-31, In Concrete Structures – Supplementary specifications, Editor Société suisse des ingénieurs et des architectes, SIA Zurich, 2013, 52 p
18. Huang, Q., Wang, C., Yang, C., Zhou, L., Yin, J., 2015. Accelerated sulfate attack on mortars using electrical pulse. Construction and Building Materials 95, 875–881.
19. Rasheeduzzafar, O.S.B., Al-Amoudi, S.N. Abduljauwad, M. Maslehuddin, 1994. Magnesium – sodium sulfate attack in plain and blended cements, ASCE Journal of Material and Civil Engineering 6, 201– 222.
20. Messad, S., Carcassès, M., Linger, L., Boutillon, L., Performance approach using accelerated test method for external sulfate attack, Proceedings of 3rd International Congress, Washington, 2010, p. 709-719
21. Cheng, Y., Sun, W., Scrivener, K., 2013. Mechanism of expansion of mortars immersed in sodium sulfate solutions. Cement and Concrete Research 43, 105‑111.
22. Rozière, E., Etude de la durabilité des bétons par une approche performantielle, Thèse de doctorat, Ecole Centrale de Nantes (2007)
23. Planel, D., Sercombe, J., Le Bescop, P., Adenot, F., Torrenti, J.-M., 2006. Long-term performance of cement paste during combined calcium leaching–sulfate attack: kinetics and size effect. Cement and Concrete Research 36, 137–143.
24. Cao, H.T., Bucea, L., Ray, A., Yozghatlian, S., 1997. The effect of cement composition and pH of environment on sulfate resistance of Portland cements and blended cements. Cement and Concrete Composites 19, 161–171.
25. Massaad, G., Rozière, E., Loukili, A., Izoret, L., 2017. Do the geometry and aggregates size influence external sulphate attack mechanism?. Construction and Building Materials 157, 778–789.
26. EN 196-1:2016, Methods of testing cement. Determination of strength, CEN, May 2016
27. B. Larbi, W. Dridi, P. Dangla, P. Le Bescop, Link between microstructure and tritiated water duffusivity in mortars: Impact of aggregates, Cem. Concr. Res. 82 (2016) 92–99
28. Kanna, V., Olson, R. A., Jennings, H. M., 1998. Effect of shrinkage and moisture content on the physical characteristics of blended mortars. Cement and Concrete Research 28, 1467-1477.
29. Lenormand, T., Rozière, E., Loukili, A., Staquet, S., 2015. Incorporation of treated municipal solid waste incineration electrostatic precipitator fly ash as partial replacement of Portland cement : Effetc on early age behaviour and mechanical properties. Construction and building Materials 96, 256-269.
30. Sahin, M., Mahyar, M., Erdogan, S. T., 2016. Mutual activation of blast-furnace slag and high-calcium fly ash rich in free lime and sulfates. Construction and Building Materials 126, 466-475.
31. Planel, D., Sercombe, J., Le Bescop, P., Adenot, F., Torrenti, J.-M., 2006. Long-term performance of cement paste during combined calcium leaching–sulfate attack: kinetics and size effect. Cement and Concrete Research 36, 137–143.
32. Zhou, Q., Glasser, F. P., 2001. Thermal stability and decomposition mechanisms of ettringite at < 120°C. Cement and Concrete Research 31, 1333‑1339
33. Trotignon, L., Peycelon, H., Bourbon, X., 2006. Comparison of performance of concrete barriers in clayey geological medium. Physics and Chemistry of the Earth 31, 610-617.
34. Monteiro, Paulo J. M., et Kimberly E. Kurtis., 2003. Time to failure for concrete exposed to severe sulfate attack. Cement and Concrete Research 33, 987‑993.
35. Lipus K., VDZ approach for testing SR cements, RILEM TC-251 SRT – External Sulfate Attack Workshop, Madrid, 25 May 2018