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Durability of concrete exposed to leaching and external sulphate attacks

E. Rozière, A. Loukili*, R. El Hachem, F. Grondin

Research Institute of Civil Engineering and Mechanics (GeM), UMR-CNRS 6183, Ecole Centrale de Nantes, France

Leaching and external sulphate attack on concrete lead to dissolution of hydration products, mainly portlandite, and in case of ingress of sulphate ions to formation of expansive products such as gypsum and ettringite. Durability of concrete exposed to these environments is still based on prescriptive specifications. The aim of the study is to provide experimental data to design performance based tests and specifications for a comparative approach. Tests have been developed to study these degradations in controlled conditions at constant pH. A leaching test has been performed on concrete. Indicators can be deduced from the leaching test and they are sensitive to the variations of potential durability. An accelerated test using a high sulphate concentration has been performed on mortars. Expansion results are sensitive to mortar mix proportions and the test could be used to qualify cements or binders in a comparative approach. Concrete specimens are exposed to external sulphate attack at two levels of sulphate concentration to provide long-term data that can be used to study the relevance of the accelerated tests and models which are being developed. Results from both series of tests show a correlation between the resistance to leaching and the resistance to external sulphate attack.

Keywords:

C. Durability
C. Sulfate attack
Leaching
D. Sulfate Resistant Cements
C. Expansion

1. Introduction

Leaching is a diffusion-reaction phenomenon which takes place when concrete is exposed to poorly mineralized or acid water. Degradation consists in dissolution of calcium and hydroxide ions out of the matrix, which causes an increase in porosity and transport properties of surface concrete [1,2]. Leaching is accelerated in neutral and acid solutions [3,4], and it may be coupled with the ingress of aggressive ions such as chloride, sulphate, magnesium [5]. These issues need to be taken into consideration in the design of concrete structures in contact with ground water—such as nuclear waste containers [6]—and also nuclear cooling towers, wastewater treatment plants and precast concrete products such as water tanks and sewage pipes. The mechanism of degradation of concrete exposed to external sulphate attack depends on exposure conditions, such as temperature [7,8], associated cation [9,10] and sulphate concentration [11–13]. The best known mechanism involves C_3A and portlandite in the cement matrix and sulphate ions [9,14–16]. The first stage of this mechanism is based on a diffusion-reaction based phenomenon. Sulphate ions react with portlandite to form gypsum, which can in turn react with the hydration products of C_3A to form ettringite. The formation of gypsum and ettringite can be expansive. During the second stage of degradation the expansive products that have filled the porosity of concrete cause swelling, damage and finally a strength loss of concrete.

The everyday durability approach of concrete exposed to leaching and external sulphate attack is prescriptive. Standards [17] are based on limiting values of the maximum water/binder ratio, minimum cement content, minimum compressive strength, and in case of sulphate attack prescriptions on binder are added. In the French standard on concrete NF EN 206-1 [17], the maximum proportion of mineral admixtures such as fly ash and slag is 15% of the mass of binder, and so-called 'sulphate-resisting' cements are required. Sulphate resistance of cements is defined in other standards [18,19]. It generally consists in limiting maximum C_3A content (5% in both standards). Such cements are designed either by increasing the C_4AF/C_3A ratio of Portland cements or by increasing the slag proportion in blended slag cements — which is contradictory to limits on binder from the standard on concrete.

However cost-effectiveness, environmental and technical issues have shown the need for performance based specifications for the same durability [20]. In existing test procedures resistance of binders to external sulphate attacks is assessed on mortar prisms. Acceleration is obtained by decreasing the volume/exposed surface ratio of specimens and increasing sulphate concentration: 34 g/L in ASTM C 1012 [21] and NF P 18-837 [22], 29.8 g/L in Wittekindt procedure [23]. But in field exposure conditions sulphate concentration is usually much lower: about 2.7 g/L in seawater [24], from 0.2 to 6 g/L in groundwater according to the definition of XA exposure classes in European standard EN 206 [17]. Mehta [25] and Brown [26] have shown the influence of pH on sulphate attack. In a laboratory study, it is typical to use only sodium sulphate, but not magnesium sulphate that would induce a coupled mechanism of degradation involving magnesium ions and CSH [9,10].

* Corresponding author.

E-mail address: ahmed.loukili@ec-nantes.fr (A. Loukili).

In this study, the effect of the exposure conditions has been taken into account to develop a representative test on concrete, using automatic control of pH and two levels of sulphate concentration (3 g/L and 30 g/L). Six concrete mixtures have been designed to study the sensitivity of the performance tests. Concrete specimens have been exposed to pH controlled leaching test and sulphate test. The corresponding cements and binders were studied by means of the test on mortar. Mass, dynamic elastic modulus (from resonance frequencies), and expansion have been monitored in order to understand the main mechanisms of degradation, and to find the most sensitive indicators of the damage degree, and the main composition parameters.

The aims of the study were: assessing the sensitivity of the test on mortar and the leaching test, and designing a representative test on concrete. The test is new because pH is automatically controlled, sulphate concentration is low (3 g/L), and it is done on concrete. pH controlled tests have been done on concrete at high sulphate concentrations (Brown [26]) and on cement pastes at low sulphate concentrations (Planel [6]). The results provided information on the mechanisms by comparing the results of the leaching test and sulphate attacks (Section 4.2.2), and analysing the results of the test from the compositional differences, for each exposure condition.

2. Characteristics of materials and mixture proportions

2.1. Cementitious materials and binders

The test on mortars was designed to assess chemical resistance of cements or binders of concrete exposed to sodium sulphate attacks. Chemical and physical properties of the cements, ground granulated blast-furnace slag (GGBS) and fly ash (FA) are given in Table 1. FA (Cordemais, France) has low calcium content and can be compared to ASTM Class F fly ash (Lawrence et al., 2005). GGBS (Moerdijk, Netherlands) complies with technical agreement (ATG) in Belgium, BRL 9325 (KIWA) and 9340 (BMC) in the Netherlands and standards NF in France. Three reference cements were used, namely:

- Portland cement CEM I 52.5 R (1) (high C₃A content: 10.6%), Beffes
- Sulphate resisting Portland cement CEM I 52.5 N PM ES (low C₃A content: 2%), Le Havre
- Sulphate resisting blended cement CEM III I 42.5 PM ES made of 62% ground granulated blast-furnace slag (GGBS), Le Havre.

Their compositions are significantly different. They may be used as reference binders to study the sensitivity of the test. Three other

binders were designed to investigate the influence of the chemical composition of binders on sulphate resistance of concrete:

- Portland cement CEM I 52.5 R (2) (high C₃A content: 7.6%), Saint Pierre La Cour
- Portland cement CEM I 52.5 R + 62% GGBS.

2.2. Mortars

The reference mixes M1, M2, and M3 were designed according to standard NF EN 196-1. The mixtures were made of three parts of normalized sand (1350 g), one part of cement (450 g) and half part of water (225 g). The six previously described binders were respectively used in M1–M6 mortars, keeping a constant w/b ratio.

M7, M8, M9 mortars mixtures are made of the three reference cements to study sensitivity of the test and they have higher w/b ratio, in order to accelerate the test. M10, M11, M12 mortars have lower w/b ratio to study the effect of an increase in compactness on resistance to external sulphate attack. The twelve mortars mixtures given in Table 2 were designed keeping the paste volume (water + binder volumes) constant.

2.3. Concrete mixtures

Six concrete mixtures were designed using the same cementitious materials (Table 3). Siliceous sand gravels were used to avoid coupled degradations due to calcium carbonate [12] in case of use of limestone aggregates. Two concrete mixtures C2 and C4 comply with two levels of prescriptive requirements (XA2 and XA3 exposure classes) from standard NF EN 206-1 [17] for exposure to leaching and sulphate attacks, in terms of minimum Equivalent Binder content (Eq. Binder) and maximum $W_{eff}/Eq. Binder$ ratio. C3 and C6 concrete mixtures do not comply with maximum $SCM/(SCM+C)$ ratio, equal to 0.15 in sulphate rich waters or soils. Binder of C5 concrete mixture is not sulphate-resisting, because its C₃A content is higher than 5%. C1 concrete mixture was made of this same cement and has high $W_{eff}/Eq. Binder$ ratio. Such mixture often leads to poor resistance to leaching and sulphate attacks [27], but C1 was designed to investigate the sensitivity of the test.

3. Experimental procedures

Concrete specimens were exposed to a leaching test and external sulphate attacks in order to assess relevance and sensitivity of these tests and related performance based indicators. Moreover a test was

Table 1
Characteristics of cementitious materials.

	Cements				Supplementary cementitious materials (SCM)	
	CEM III N	CEM I N	CEM I R	CEM I R	GGBS	Fly Ash
	PM ES	PM ES	(1)	(2)		
<i>Chemical analysis (%)</i>						
SiO ₂	28.60	21.25	19.45	20.40	34.49	52.5
Al ₂ O ₃	8.80	3.47	5.31	4.70	13.19	27.9
Fe ₂ O ₃	1.07	4.23	2.50	2.95	0.40	5.6
CaO	50.40	64.95	63.06	64.10	41.03	2.2
SO ₃	2.27	2.65	3.71	3.60	0.10	0.6
<i>Compound composition of clinker (%)</i>						
C ₃ S	66.4	73.5	65.7	63.6	–	–
C ₂ S	5.6	5.5	10.0	13.4	–	–
C ₃ A	11.4	2.0	10.6	7.6	–	–
C ₄ AF	5.4	12.9	8.0	9.4	–	–
<i>Physical properties</i>						
Blaine fineness (cm ² /gr)	4300	3650	4285	4130	4620	3840
Normal comp. strength (MPa)	57.9	62.6	65.5	65.5	–	–

Table 2
Proportions of mortar mixtures.

(kg/m ³)	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
Sand	1484	1494	1490	1490	1490	1490	1484	1494	1490	1484	1494	1490
Cement												
CEM III PM ES	495						419			591		
CEM I PM ES		498				368		420			597	
CEM I R (1)			497						420			593
CEM I R (2)				497	190							
GGBS					316							
FA						158						
Superplasticizer					4.4					8.8	8.9	9.9
W_{eff}	247	249	248	248	237	231	272	273	273	207	209	208
$W_{eff}/Eq. Binder$	0.50	0.50	0.50	0.50	0.50	0.50	0.65	0.65	0.65	0.35	0.35	0.35

performed on mortars to design a performance test for binders exposed to sulphate attack (Table 4).

3.1. Leaching test

The procedure was adapted from existing tests [6,28]. Two identical experimental devices were built in order to study the repeatability and to use the test in a comparative performance based approach (Fig. 1). For each test a 25-mm thick specimen was sawed from a $\varnothing 11 \times 22$ cm specimen. The specimen was circumferentially coated with a waterproof vinyl ester resin, and hence was exposed to leaching only on its two plane surfaces.

Specimens were immersed in 1.5 L of demineralised water. The temperature was kept constant at 20 °C using a jacketed beaker of 2 L and a regulator. As pH tends to increase because of the dissolution of portlandite $Ca(OH)_2$, it is controlled by adding appropriate volumes of 0.5 mol/L nitric acid solution, through a controlled burette. The set point of pH was 5, and the measured value was 5.0 ± 0.1 . The solution was renewed whenever 30 mL of nitric acid had been added. The calcium concentration was assessed by atomic absorption spectrometry [29]. C2, C3, C4, C5, C6(1), C6(2) concrete samples were tested

Table 3
Proportions of concrete mixtures.

Exposure classes (kg/m ³)	X0		XA2		XA3	
	C1	C2	C3	C4	C5	C6
<i>Siliceous gravels Palvadeau</i>						
12.5/20	365	374	358	372	374	366
8/12	268	275	264	274	275	269
4/8	410	421	403	419	421	412
<i>Siliceous sand Palvadeau</i>						
2/4	56	57	55	57	57	56
1/4	238	244	234	243	244	239
0.5/1	130	133	127	132	133	130
0.315/1	192	197	189	196	197	193
0/0.315	103	106	102	105	106	104
0/0.160	22	23	22	23	23	23
<i>Cement (C)</i>						
CEM III PM ES	-	-	-	385	-	-
CEM I PM ES	-	352	280	-	-	-
CEM I R (2)	280	-	-	-	385	156
<i>SCM</i>						
Fly ash Cordemais ($k=0.6$)	-	-	120	-	-	-
GGBS ECOCEM ($k=0.9$)	-	-	-	-	-	254
Effective water (W_{eff})	205	174	174	154	154	154
Superplasticizer	0	0.73	1.29	4.14	3.16	3.38
Eq. Binder content (C+k.SCM)	280	352	352	385	385	385
$E_{eff}/Eq. Binder$	0.73	0.49	0.49	0.40	0.40	0.40
SCM/(SCM+C)	0	0	0.30	0	0	0.62
Volume of paste V_p (L/m ³)	296	286	308	282	278	293

at 43, 56, 42, 68, 45, 38 days after batching respectively. A nitrogen flow was used to avoid carbonation.

3.2. External sulphate attacks

3.2.1. Tests on mortars

The procedure followed for the test on mortar is close to those described in French standard NF P 18-837 [22] and ASTM standard C 1012 [21]. It consists in immersing prismatic mortar specimens in concentrated sodium sulphate solution. For each mortar mixture, six $4 \times 4 \times 16$ cm³ prismatic specimens and six $2 \times 2 \times 16$ cm³ specimens were cast and sealed cured for 24 h. They were stored in water for 14 days then for 14 days at 40 °C. Three control specimens were vacuum saturated with tap water and immersed in water and three others specimens were saturated with sodium sulphate solution and immersed in the solution. The sulphate concentration is 30 g/L. The solution was prepared using demineralised water and renewed once a month. $2 \times 2 \times 16$ cm³ specimens have gauge studs to measure expansion with length comparators. The elastic modulus was determined on $4 \times 4 \times 16$ cm³ prisms with a Grindosonic apparatus. This device gives the frequency of a vibration created by a slight shock on the sample. The elastic modulus is calculated from this frequency with the Spinner and Teft model [30]. All tests were carried out on three samples and the given results are average values.

3.2.2. Tests on concrete

$7 \times 7 \times 28$ cm³ prismatic concrete specimens were sealed cured until they reach 50% of required compressive strength (NF EN 206-1) for the corresponding exposure class (X0, XA2, XA3) and stored at 20 °C and 50% RH. After 28 days they were immersed in two different sodium sulphate solutions [31]. Solutions were made of demineralised water and sodium sulphate. The sulphate concentration of the first solution was 3 g/L, and pH is controlled using 0.02 mol/L sulphuric acid solution. The sulphate concentration of the second solution was 30 g/L, and pH is controlled using 44 g/L sodium sulphate + 0.04 mol/L sulphuric acid solution. Solutions were renewed every month. Mass, length and elastic modulus of concrete samples were monitored.

Table 4
Experimental program.

		Mortar	Concrete
External sulphate attacks	Specimens	Prisms: $2 \times 2 \times 16$ cm ³ , $4 \times 4 \times 16$ cm ³	Prisms: $7 \times 7 \times 28$ cm ³
	Sulphate concentration [SO ₄ ²⁻]	30 g/L	3 g/L, 30 g/L
Leaching	Specimens	-	Cylinder: $\varnothing 11 \times 2.5$ cm

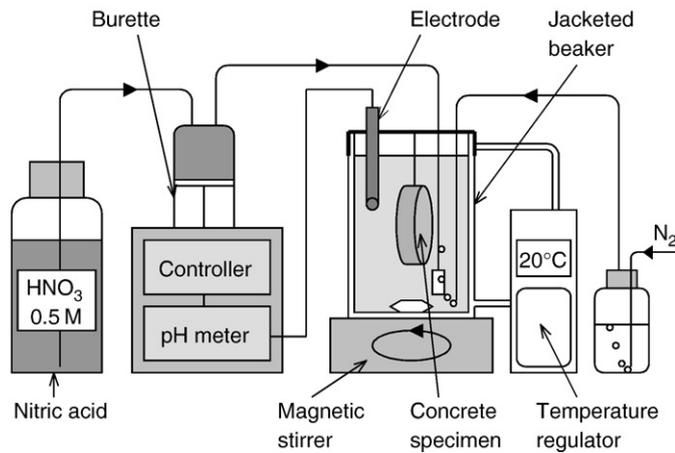


Fig. 1. Schematic diagram of leaching test.

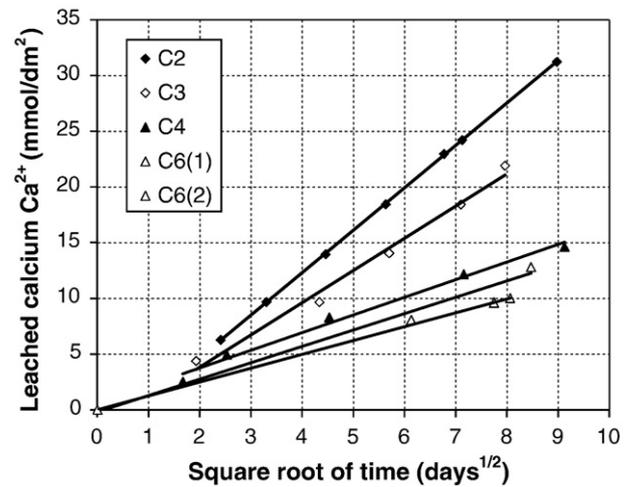


Fig. 3. Leached calcium ions.

4. Results and discussion

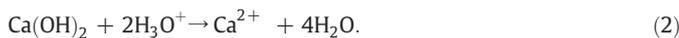
4.1. Results of leaching tests

The quantity of leached hydroxide ions was assessed through the added volumes of nitric acid HNO_3 solution, and that of leached calcium by the titration of the solutions. These quantities are plotted against square root of time in Figs. 2 and 3.

The parameters of leaching kinetics may be deduced from quantity of leached ions versus square root of time curves. Steady state was assumed to be reached after 1 day. Corresponding parameters are given in Table 5, for the following Eq. (1):

$$N(t) = a\sqrt{t} + b. \quad (1)$$

Ratios of leaching rates $a_{\text{OH}}/a_{\text{Ca}}$ are close to 2 (Table 5) suggesting leaching had mainly come from dissolution of portlandite $\text{Ca}(\text{OH})_2$ (Eq. (2)).



Ratios are actually above 2, so a part of leached calcium ions could come also from CSH.

After taking out from immersion phenolphthalein solution was sprayed over a fresh fracture to measure the damaged depth using the

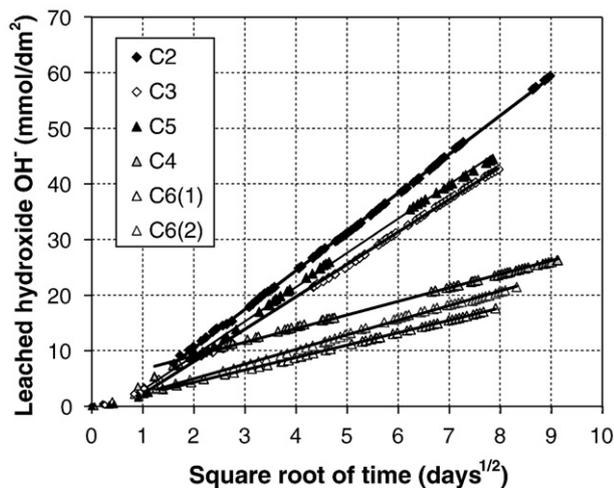


Fig. 2. Leached hydroxide ions.

coloration front. Results in Table 6 show that corroded layer is very thin, for all concrete mixtures, so a more precise and sensitive criterion was looked for. Assuming that calcium ions only came from binder and that no portlandite remained in corroded layers, equivalent damaged depths may be calculated, dividing the total amount of leached calcium by the theoretical initial total calcium content of binder. From experimental data of the leaching test and CaO content of the cementitious materials, the following ratio can be calculated and give an equivalent damaged depth (*EDD*). The Total leached calcium is the ratio of the total leached calcium on specimen surface area (in mol/m^2) and Initial calcium content in binder is in mol/m^3 .

$$EDD = \frac{\text{Total leached calcium}}{\text{Initial calcium content in binder}}. \quad (3)$$

Equivalent damaged depths of C3 and C5 concrete samples were assessed assuming a ratio of leaching rates $a_{\text{OH}}/a_{\text{Ca}}$ equal to 2.

From microstructural analyses on concrete specimen after the same testing procedure, the equivalent damaged depth would actually underestimate the damaged depth, because the corroded layer was not totally decalcified, which was an assumption of the previous calculation [29].

The amounts of leached calcium or hydroxide ions can be considered as criteria for a comparative approach of durability of concrete. The

Table 5
Parameters of leaching kinetics.

	C2	C3	C4	C5	C6 (1)	C6 (2)	
OH	a ($\text{mmol}/\text{dm}^2/\text{d}^{1/2}$)	6.97	5.82	2.45	6.17	2.23	2.64
	b (mmol/dm^2)	-3.44	-3.59	4.19	-3.23	-0.15	-0.35
Ca	a ($\text{mmol}/\text{dm}^2/\text{d}^{1/2}$)	3.81	2.90	1.59	-	1.24	1.48
	b (mmol/dm^2)	-2.95	-1.97	0.58	-	0	-0.21

Table 6
Experimental and equivalent damaged depths.

	C2	C3	C4	C5	C6 (1)	C6 (2)
Total leached calcium at 60 days (mmol/dm^2)	26.6	21.0	12.9	22.3	9.1	10.5
Initial calcium content in binder (mol/dm^3)	4.08	3.33	3.47	4.41	3.65	3.65
Equivalent damaged depth <i>EDD</i> (mm)	0.65	0.63	0.37	0.51	0.25	0.29
Experimental damaged depth <i>ExpDD</i> (mm)	0.5	0.5	<0.5	<0.5	<0.5	<0.5



Fig. 4. M9 mortar specimens after 105 and 150 days in 30 g/L sulphate solution.

leaching rates of C6 (1) and C6 (2) concrete specimens were 8.4% higher or lower than the mean value for the two tests, which was $2.44 \text{ mmol/dm}^2/\text{day}^{1/2}$, so significant differences may be deduced from experimental results.

Leaching increased with an increase in Water/Binder ratio, which can be explained by corresponding variations of porosity and diffusivity. But this does not account for all the differences. C3 should have a better behaviour than C2 concrete, and leaching rate has reduced by 18%. So incorporating 30% of FA in binder would improve resistance to leaching, and behaviour would not only depend on porosity but on chemical composition of binder. Blended cements or binder incorporating such pozzolanic materials actually produce less portlandite, with equal or enhanced compactness of the matrix.

Among the concrete tested, the concrete with high amounts of GGBS (62%) leads to good resistance to leaching. C4 and C6 concrete mixtures showed the lowest leaching rates and total amounts of leached calcium and hydroxide ions. They have the same leaching rates (respectively 2.45 and $2.44 \text{ mmol/dm}^2/\text{day}$). So including GGBS in concrete mixture instead of using blended cement had not significant effect with these materials.

Finally three indicators can be assessed from the test, namely: the Total leached calcium at the end of the test, the Experimental Damaged Depth and the Equivalent Damaged Depth. For a given type of aggregates, classifications of performances based on these three indicators were the same. Equivalent Damaged Depth is assessed from the hypothesis that the calcium is totally leached in damaged depth. The good correlation between the Experimental Damaged Depth and the Equivalent Damaged Depth suggests that the hypothesis is mainly true. Classifications of performances from the first indicator, Total leached

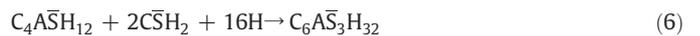
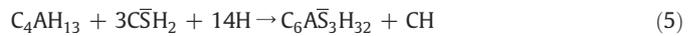
calcium, are the same because the variations of total leached calcium are higher than the variations of initial calcium content. Higher initial calcium concentrations in binder came from lower water/cement ratios and lower diffusivities and thus lead to better resistance to leaching.

4.2. Results of external sulphate attack tests

We can suppose sulphate ions are likely to react with portlandite and C_3A -rich hydration products, according to the following equations [15]:



Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is referred to as $\text{C}\bar{\text{S}}\text{H}_2$ and H_2O (H) and ettringite as $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$ in the following equations:



4.2.1. External sulphate attacks on mortars

As shown on Fig. 4, some samples have shown the typical expansion and cracking of concrete exposed to sodium sulphate

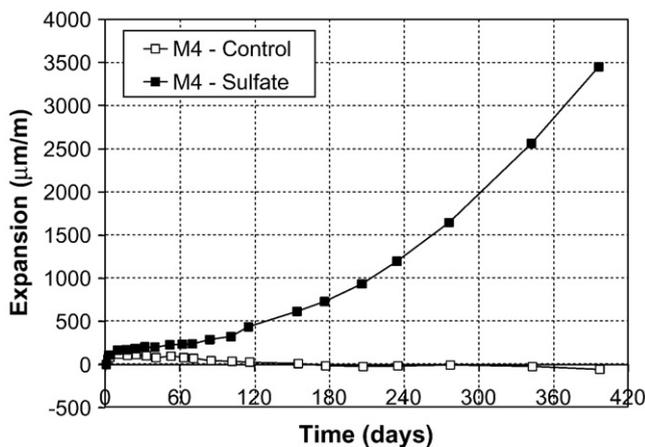


Fig. 5. Expansion of $2 \times 2 \times 16 \text{ cm}^3$ specimens.

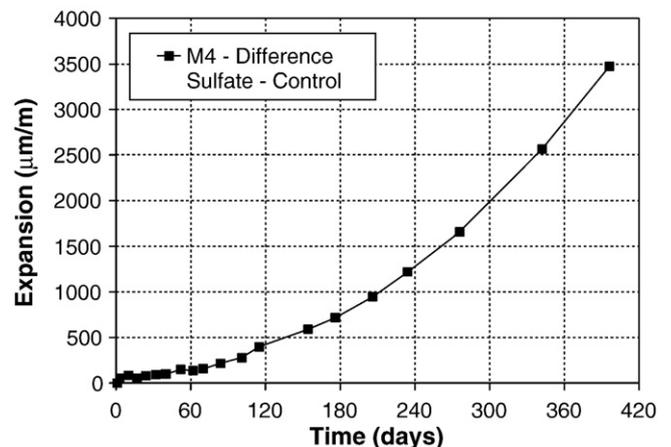


Fig. 6. Expansion of $2 \times 2 \times 16 \text{ cm}^3$ specimens. Difference between sulphate and control specimens.

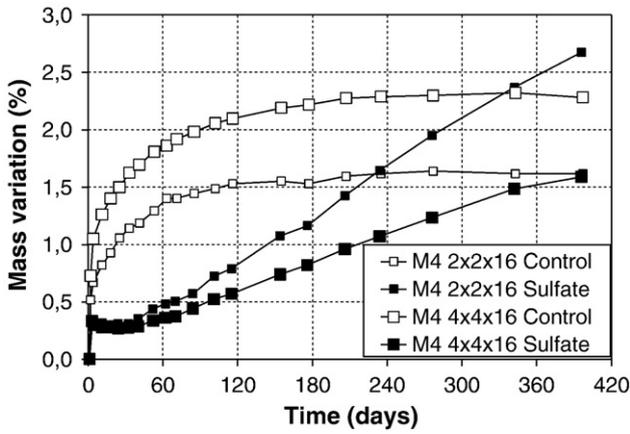


Fig. 7. Mass variations of mortar specimens.

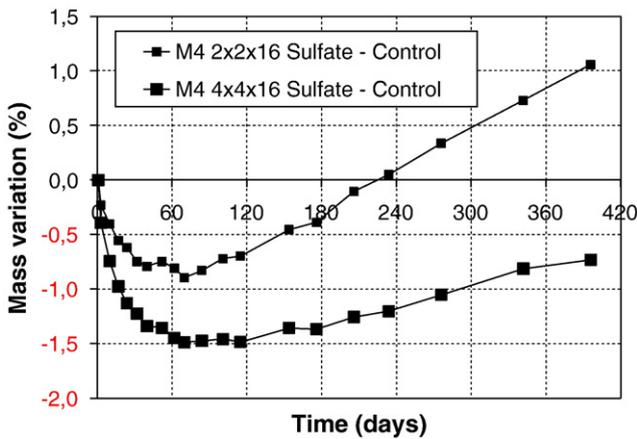


Fig. 8. Mass variations of mortar specimens. Difference between sulphate and control specimens.

solution with high sulphate concentration, i.e. equal to 20 g/L or higher [8].

Expansion was observed before cracking by the monitoring of length (Figs. 5 and 6) and mass (Figs. 7 and 8). As absorption of water and hydration are likely to occur after immersion, differences between measures on control specimens and specimens exposed to sulphate solution were calculated to focus on the effects of sulphate ions. They are plotted in Figs. 6 and 8. Relative mass decrease occurs during the period of latency, when no significant expansion occurred. The mass decrease is due to leaching. The mass increase is due to swelling caused by gypsum and/or ettringite formation in damaged mortar specimens. As the sulphate attack is external, the effect of the Exposed surface/Specimen volume ratio is important and this can be seen in Figs. 4, 7 and 8, where damage and mass increase are greatest in the specimens with the higher surface/volume ratio.

Elastic modulus (Fig. 9) does not appear as a sensitive indicator of damage during the first stage, as the modulus of attacked specimens remains equal or higher than modulus of control specimens even if significant expansion and damage can be observed. Lee et al. [32] and Sahmaran et al. [27] have also shown the positive effect of sulphate attack on mechanical properties, before they finally decrease. Decrease of elastic modulus became significant after about 120 days (Figs. 9 and 10), but mass variation appeared earlier (Fig. 7) so this would be a better indicator for a performance test.

Mortar mixtures M1 to M6 were designed keeping water/binder ratio and paste volume constant. Mass variations and expansions of these mortars are plotted in Figs. 11 and 12. Even mortar including

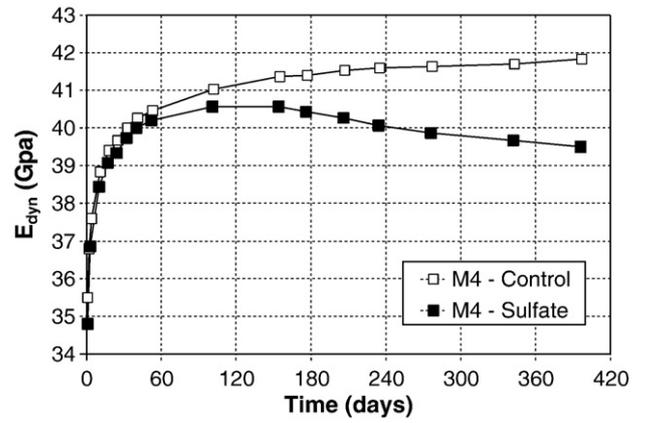


Fig. 9. Elastic modulus of $4 \times 4 \times 16 \text{ cm}^3$ specimens.

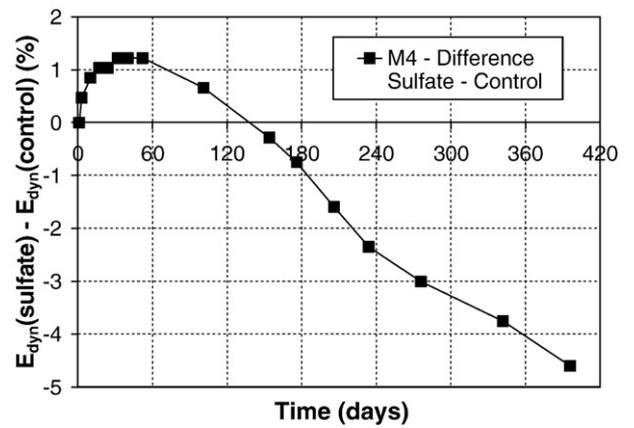


Fig. 10. Elastic modulus of $4 \times 4 \times 16 \text{ cm}^3$ specimens. Difference between sulphate and control specimens.

sulphate resisting cement (M2) shows significant expansion (Fig. 12), which has already been observed in other studies using the same kind of test on mortar [27]. Tian and Cohen [33] have shown that gypsum could also cause expansion in sulphate environments. So analysis of microstructure is necessary to know whether expansion is actually due to ettringite. Irassar [14] has found high gypsum concentration in the outer layer of damaged specimens by means of XRD analysis. An ettringite inner layer has also been found on the same samples, but

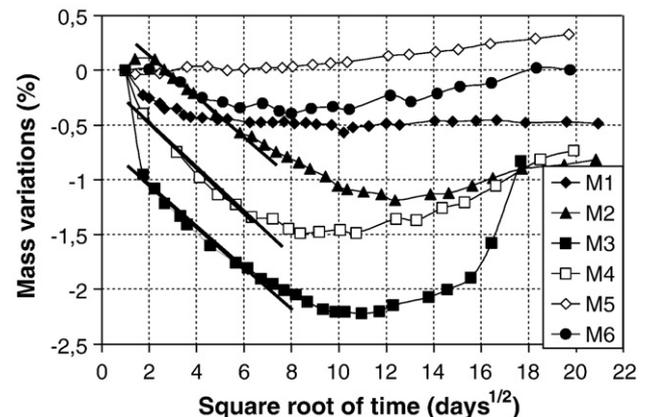


Fig. 11. Mass variations of $4 \times 4 \times 16 \text{ cm}^3$ specimens. Difference between sulphate and control specimens. Water/Binder = 0.50.

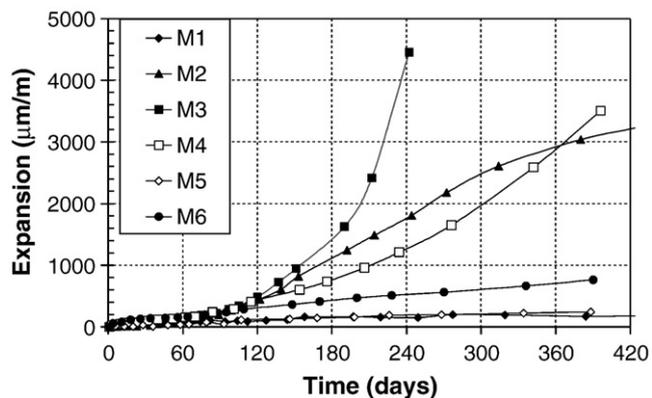


Fig. 12. Expansion of $2 \times 2 \times 16 \text{ cm}^3$ specimens. Difference between sulphate and control specimens. Water/Binder = 0.50.

gypsum could actually play an important part in the mechanism of degradation at such high sulphate concentrations.

The two stages of the degradation may be distinguished in Figs. 11 and 12. The first step corresponds to the period of latency, when no significant expansion can be measured. The second stage corresponds to significant expansion. It starts at about 60 days for M4 mortar specimens.

The difference between the mass variations of control and damaged specimens is plotted against the square root of time, which shows a linear dependency. This can be clearly seen for mortars M2, M3, and M4. That corresponds to leaching and diffusion-reaction processes between sulphate solution and hydration products, mainly portlandite $\text{Ca}(\text{OH})_2$ [6]. This could explain why the cements used in

mortars M2, M3, and M4 showed the highest expansion, even if cement used in M2 is considered as sulphate resisting. The three cements actually have approximately the same proportion of CaO and high proportions of C_3S . They produce comparatively greater amounts of portlandite on hydration than blended cements or binders. Leaching of portlandite can thus increase ingress of sulphate ions in cement matrix. Moreover reaction with sulphate is likely to produce more gypsum (CaSO_4) and more ettringite ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), which are responsible for expansion and damage.

Gypsum has actually been observed on cracked mortar samples. Fig. 13 shows scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) analysis on M4 polished mortar sample. EDS analysis (Table 7, Fig. 14) was performed at accelerating voltage of 20 keV and takeoff angle of 37° . High silicon concentrations come from siliceous aggregate and calcium comes from cement paste. High concentrations of sulphur can be observed in cracks, especially between paste and aggregates. Normalized weight concentrations and atomic proportions given by quantitative analysis are closed to composition of gypsum CaSO_4 , and Ca/S ratio is equal to 1.1. This confirms the part played by gypsum in expansion due to sulphate attacks.

Fig. 15 confirms the influence of the chemical composition of binder on expansion of mortar. Expansion after 180 and 360 days has been plotted as a function of the sum of CaO and Al_2O_3 proportions, as these two oxides are the main compounds of C_3S and C_3A , so they potentially lead to production of ettringite and gypsum in sulphate-rich environments. Two behaviours can be distinguished. Portland cements, i.e. the two high- C_3A cements and the sulphate-resisting cement, have the same $\text{CaO} + \text{Al}_2\text{O}_3$ content (68.4%). They showed significant expansions for water/binder ratios equal or higher than 0.5. Even if C_3A content is known as a major parameter, this result

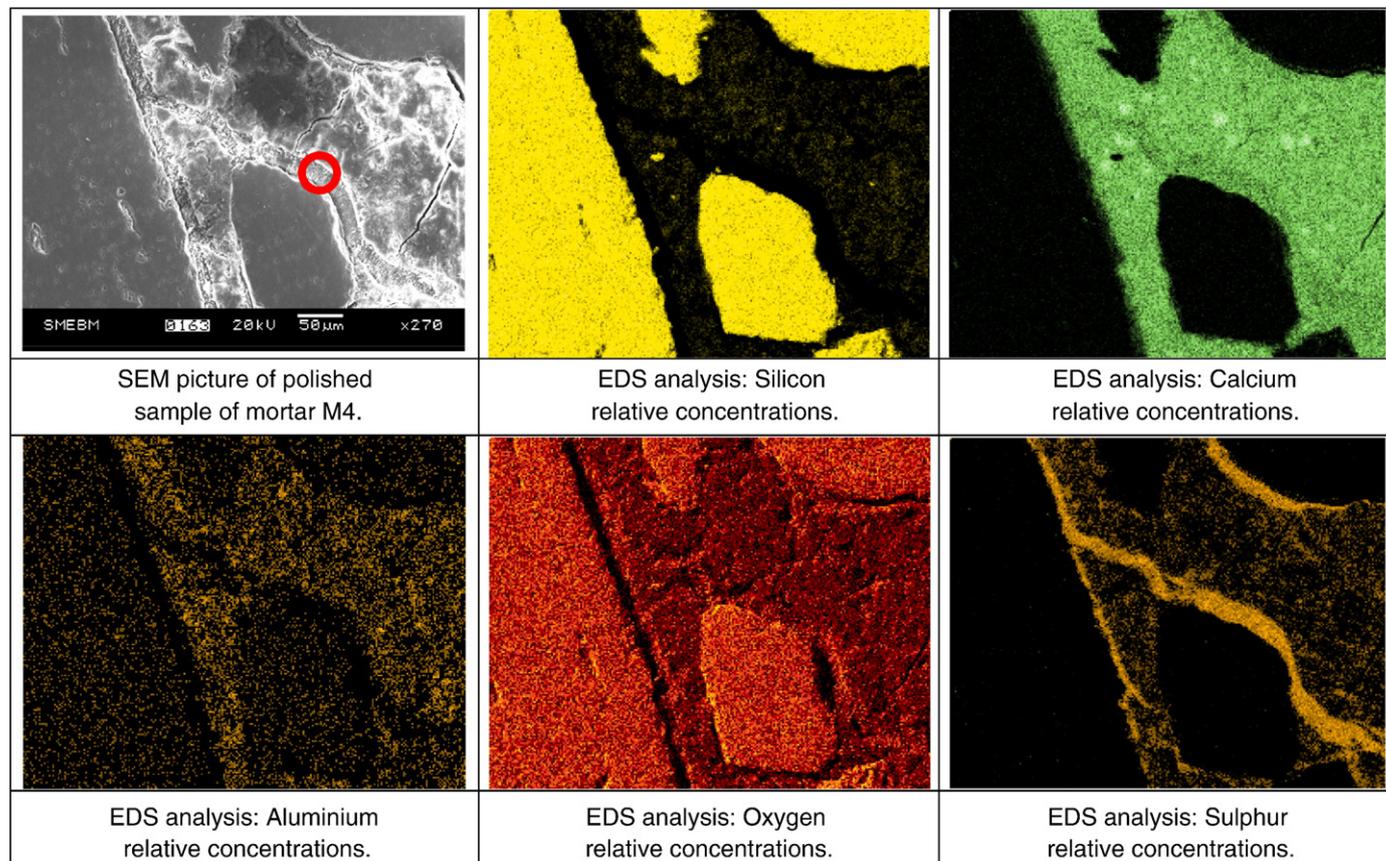


Fig. 13. Scanning electron microscopy and energy dispersive spectroscopy analysis on M4 mortar sample.

Table 7

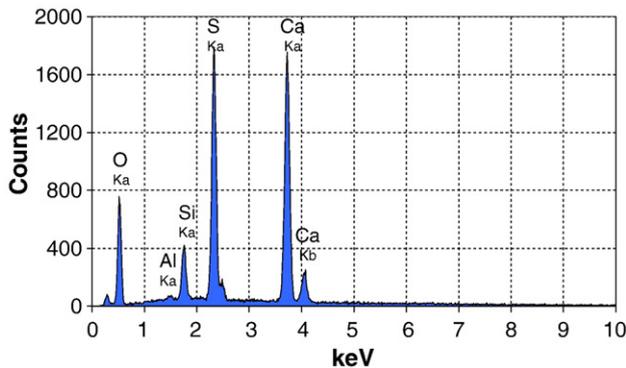
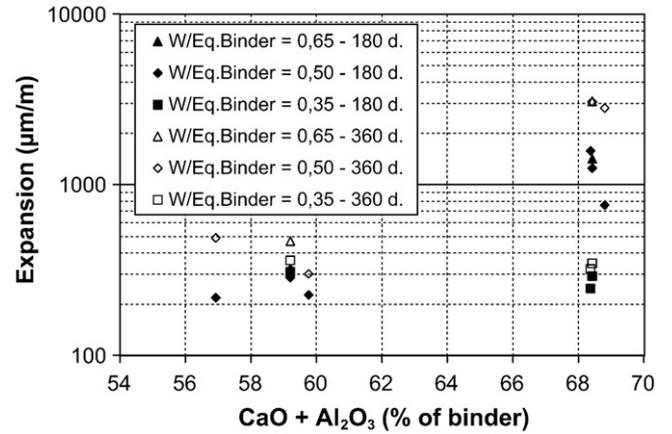
EDS analysis on M4 mortar sample (circled zone): quantitative analysis.

Element	Normalized conc. (wt.%)	Precision	Atomic prop. (%)	Line
O	58.7	3.75	75.8	K line
Al	0.31	0.16	0.23	K line
Si	3.70	0.34	2.72	K line
S	15.7	0.59	10.2	K line
Ca	21.7	0.78	11.2	K line
Total	100.00		99.99	

suggests that C_4AF could also play an important part. Mortars made of the same cements but with lower water/binder ratio (0.35) did not show any significant expansion. Reducing the water/binder ratio actually improves strength and resistance to the ingress of the sulphate ions by diffusion [27,34]. The slag cement and the binders made of Portland cement and slag (62%) or fly ash (30%) showed much lower expansion, even for high water/binder ratios [35–37]. But expansion of M6 (30% FA, $w/b = 0.50$) and M7 (62% GGBS, $w/b = 0.65$) had not stabilized after 420 days, so w/b ratio and chemical composition of binder are both important parameters and slight variations can completely change behaviour of mortars or concrete, from stabilization to unlimited expansion. The water–binder ratio influences the diffusivity and the strength of mortar or concrete. The $CaO + Al_2O_3$ content is related to the potential amount of gypsum and ettringite and the forces due to formation of these products. The result of the test is global and influenced by both factors, namely: the forces coming from the formation of expansive products, and the resistance (tensile strength) of the material. The diffusivity influences the kinetics. Slight changes of composition parameters can thus significantly affect the potential expansion or the strength, thus the behaviour of mortar.

The behaviours distinguished in Fig. 15 are consistent with expansion data from ASTM C 1012 tests. According to ASTM Subcommittee C01-29 [38], cements satisfying the expansion limits of 0.10% (1000 $\mu\text{m}/\text{m}$) and 0.05% (500 $\mu\text{m}/\text{m}$) at 26 weeks are considered as moderate sulphate resistant and high sulphate resistant, respectively and the expansion limits of 0.10% (1000 $\mu\text{m}/\text{m}$) at 52 weeks are considered as high sulphate resistant [27]. But expansion at a given time does not give information on future stability of mortar or concrete. Monteiro and Kurtis [39] have proposed a predictive approach based on experimental asymptotic analysis, from the 40-year study on concrete conducted by the U.S. Bureau of Reclamation (USBR).

During the first stage of sulphate attacks, leaching occurs and the dominant phenomenon is the diffusion-reaction as shown in Fig. 11. During the second stage of expansion, other phenomena occur such as the formation of expansive products, damage and, in some cases,

**Fig. 14.** EDS analysis on M4 mortar sample (circled zone): spectrum.**Fig. 15.** Influence of chemical composition of binder on expansion of mortar.

coupling with hydration and healing. The aim of this approach is to obtain similitude laws for phenomena from experimental results [39]. The scaling law for the expansion ε of concrete or mortar is expressed as follow:

$$\varepsilon = K(t - t_0)^\alpha \quad (8)$$

where K is a constant, t the time, t_0 the effective origin of time and α the scaling exponent. α can be assessed by plotting $\log(\varepsilon)$ as a function $\log(t)$. Therefore the curve $\varepsilon^{1/\alpha}$ versus t is linear (Fig. 16). The value of t_0 is given by the intercept with the horizontal axis. The same graph provides the initiation time t_i , which represents the initiation of the expansion stage.

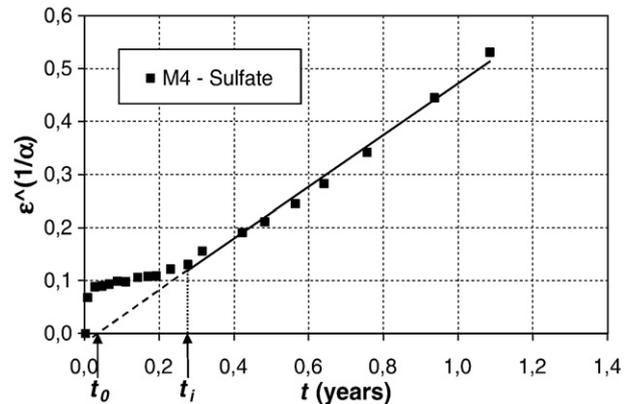
Mortars M1, M5, M10, M11 and M12 did not show expansion. Instead, they show saturation behaviour, as expansion increases but remains limited. Forces due to expansion of the products of sulphate attack are lower than the strength of the material. The saturation process repeats itself (Fig. 17). It was defined by the following equation:

$$\varepsilon = \varepsilon_{lim}(1 - e^{-\beta t}). \quad (9)$$

Based on data from the USBR tests on concrete, Monteiro and Kurtis [39] defined a *potential damage Pd* to predict the initiation time or saturation behaviour from the composition of concrete and cement:

$$Pd = C_3A^{1.39}C_3S^{2.9}C_4AF^{0.77}(w/c)^{7.80}. \quad (10)$$

As shown in Fig. 18, this model gives a good assessment for the behaviour of mortars exposed to the same kind of test. It is difficult to

**Fig. 16.** Assessment of t_0 and t_i of self-similar curve.

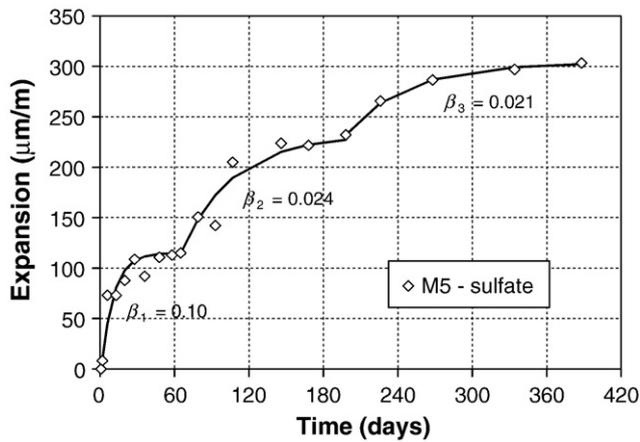


Fig. 17. Saturation curves of mortar M5.

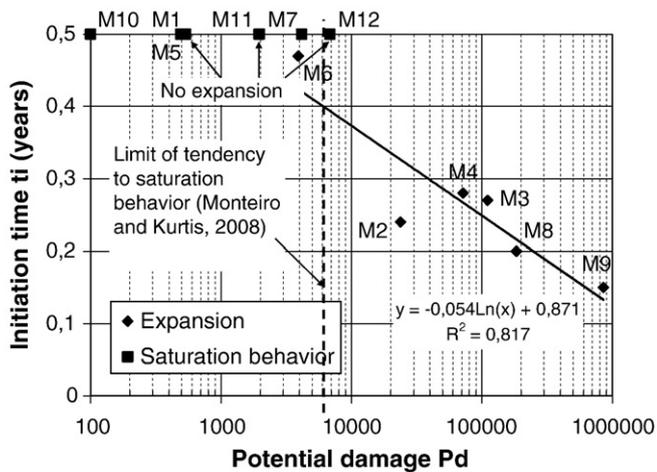


Fig. 18. Analysis of expansion data by scaling law.

find the limit of tendency to saturation behaviour. For instance, M12 mortar has not shown significant damage but saturation behaviour, whereas M6 mortar has shown self-similar behaviour. So slight changes in cement properties or w/b can significantly affect performance of concrete exposed to sulphate attacks according to this test procedure [27,39]. All expansion data are presented in Table 8.

Results from this study on mortars are consistent with other studies on the same test. As the sulphate concentration could modify the conditions of sulphate attack, especially the relative amounts of

Table 8
Analysis of expansion data.

	α	t_0	t_i	Pd
	Measured	Origin of time	Initiation time	Potential of damage
M1	-	-	-	536
M2	1.70	0.016	0.24	22,315
M3	2.47	0.019	0.27	110,622
M4	1.68	0.032	0.28	71,718
M5	-	-	-	492
M6	1.16	0.001	0.47	3671
M7	-	-	-	4150
M8	1.44	0.048	0.20	172,729
M9	3.08	0.045	0.15	856,252
M10	-	-	-	33
M11	-	-	-	1382
M12	-	-	-	6849

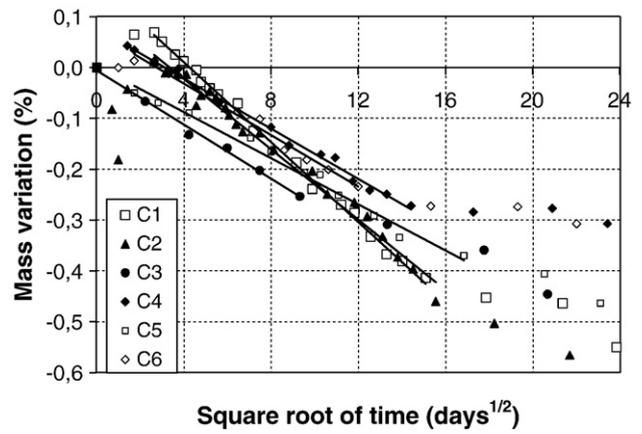


Fig. 19. Difference of mass variations of immersed concrete specimens. $[SO_4^{2-}] = 3 \text{ g/L}$. Reference: mass before immersion.

gypsum and ettringite, the tests on concrete were designed to take into account sulphate concentration and control of the pH of the solution.

4.2.2. External sulphate attacks in concrete

The mass of control and attacked specimens was monitored. Control specimens stored in tap water showed a slight mass increase, which corresponds to hydration, whereas specimens stored in sulphate solution showed much lower increase or slight loss of mass. In order to separate the effect of sulphate attack from phenomena of absorption and hydration, differences of relative mass variations are plotted against square root of time in Fig. 19. The graph shows linear variations, which can be due to diffusion-reaction phenomenon, such as leaching and ingress of sulphate ions [6].

In order to compare these variations to the kinetics assessed from the leaching test, the kinetics from Fig. 19 were converted into loss of portlandite per unit area of sample (Table 9). They are of the same order of magnitude and they show the influence of composition parameters such as water/binder ratio and chemical composition of the binder. Significant differences appear for concrete mixtures C2, C3, and C5. The corresponding binders are mainly made of Portland cement.

Damaged depths can not be deduced only from leaching kinetics. As the sulphate test is still in progress, it is not possible to use a colorimetric indicator on a fracture of specimens. Visual observation can bring useful information on the degree of degradation, in a comparative approach [14]. Classification is given in Table 10 and shows good correlation with the classification from leaching test (Table 6).

The cement used in concrete mixtures C1B and C5B (see Fig. 21) is the high- C_3A cement used in mortars M3, M9, and M12 but concrete mixtures are the same as C1 and C5. After immersion, expansion is due to absorption of water and depends on the magnitude of drying shrinkage before test. After this first stage, neither monitoring of mass nor monitoring of length shows expansion due to sulphate attack at both sulphate concentrations (Figs. 20 and 21). Even if controlled pH accelerates degradation [40], the sulphate attack is external and an

Table 9
Kinetics of loss of mass, from sulphate attack test and leaching test.

	Sodium sulphate solution, $[SO_4^{2-}] = 3 \text{ g/L}$, $\text{pH} = 7$		Nitric acid solution, $\text{pH} = 5$
	k (mass %/day $^{1/2}$)	$a_{Ca(OH)_2}$ (mmol/dm 2 /day $^{1/2}$)	$a_{Ca(OH)_2}$ (mmol/dm 2 /day $^{1/2}$)
C1	0.039	2.01	-
C2	0.035	1.83	3.81
C3	0.027	1.41	2.90
C4	0.025	1.33	1.59
C5	0.023	1.22	3.27
C6	0.025	1.32	1.36

Table 10
Classification of performances from external sulphate attack test on concrete.

	Time of immersion	Surface appearance	Classification of performances
C1	597	Porous – severe attack	5
C2	609	Porous – severe attack	5
C3	463	Slight attack	3
C4	578	Very slight attack	1
C5	560	Moderate attack	4
C6	519	Very slight attack	1

increase in volume/surface ratio of specimens causes a corresponding increase in initiation time of degradation of paste [6], mortar (Fig. 4) and concrete specimens [41,42]. The test is actually not meant to classify performances of concrete mixtures by accelerated degradation, but to provide data on behaviour of concrete exposed to sulphate attack in realistic and controlled conditions. So these data can be useful to conclude on relevance of accelerated tests or models of external sulphate attacks [43] based on the evolution of the microstructure of concrete [44].

5. Conclusions

The aim of the study was to provide comparative performance-based tests and indicators to assess durability of concrete exposed to leaching and external sulphate attacks. Sensitivities of existing tests have been investigated and a new test has been developed for external sulphate attacks on concrete.

- Leaching test on concrete has shown good sensitivity: varying water/binder ratio and chemical composition of binder lead to significant changes in the behaviour of concrete. Three indicators can be assessed from test data, namely: total leached calcium at the end of the test, experimental damaged depth and equivalent damaged depth (for siliceous aggregates). This test is under evaluation for standardization.
- Test on mortar could be used to qualify binders, for a given water/binder ratio and volume of paste. Conditions of exposure are not totally controlled and high sulphate concentration could be responsible for decreasing potential durability of sulphate-resisting Portland cements because of gypsum formation. The test is sensitive enough to show different behaviours of the studied reference binders, namely: high-C₃A Portland cement, low-C₃A sulphate-resisting Portland cement, and sulphate-resisting slag cement. Experimental asymptotic analysis developed by Monteiro and Kurtis [39] from long-term study on concrete has been shown to be reliable to analyse data from the test.

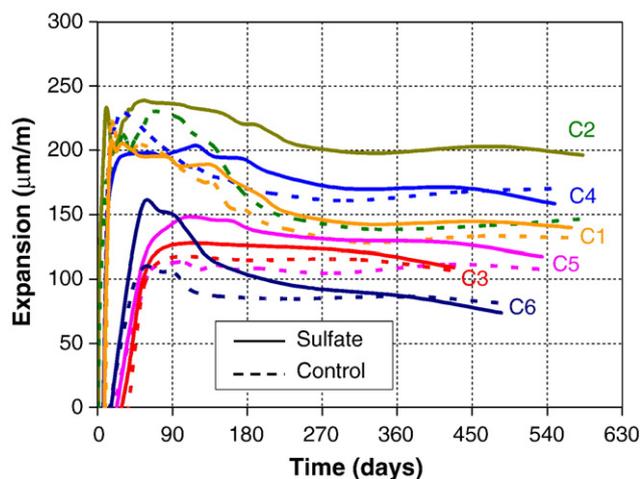


Fig. 20. Expansion of immersed concrete specimens. $[SO_4^{2-}] = 3 \text{ g/L}$.

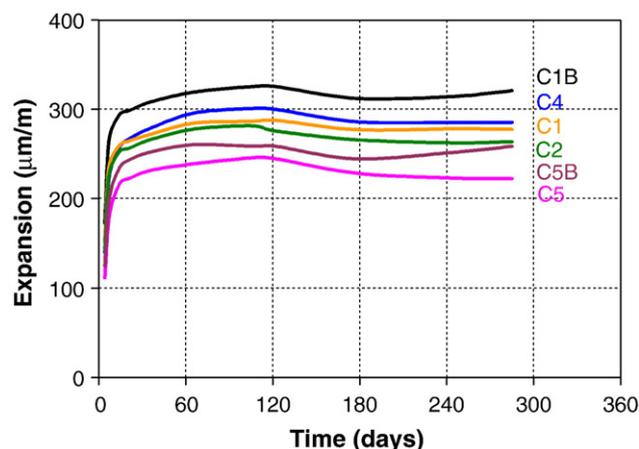


Fig. 21. Expansion of immersed concrete specimens. $[SO_4^{2-}] = 30 \text{ g/L}$.

- A new test has been developed to expose concrete to external sulphate attack in controlled conditions: pH is automatically controlled and two tests are still in progress at two sulphate concentrations (3 g/L and 30 g/L SO_4^{2-}). The long-term objective is to provide data to study relevance of the accelerated tests and models which are being developed.
- As classifications of performances are consistent, studies of external sulphate attack on mortars and concrete have both shown that leaching plays a predominant role. Leached portlandite would facilitate ingress of sulphate ions and produce reactants to form expansive products such as gypsum and ettringite. Portlandite comes from hydration of C₃S and C₂S. So substitution of high-C₃S Portland cement by 30% of fly ash improved behaviour of mortar or concrete exposed to leaching and sulphate attack. The best behaviour was obtained when Portland cement was substituted by 62% of ground granulated blast-furnace slag, either by using commercial slag cement or by blending Portland cement and slag in concrete.

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