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External sulphate attack of sprayed mortars with sulphate-resisting cement: influence of accelerator and age of exposition

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ABSTRACT

This work evaluates the influence of the accelerator type, the cement type and age of exposure on the degradation mechanism and the durability of sprayed mortars subjected to external sulphate attack (ESA). Cores and prisms were extracted from panels sprayed with 8 mortar compositions (with 2 sulphate-resisting cement types and 4 setting accelerators) and then exposed to a sulphate solution at the ages of 7 or 28 days for 400 days. The evolution of the ESA was assessed through XRD, SEM, compressive strength, dimensional variation and ultrasonic pulse velocity. Results show that alkaline accelerators increase drastically the vulnerability of the matrix to the ESA. The degradation is enhanced by the higher solubility of aluminate phases and the increased formation of expansive phases. Results reveal that the use of sulphate-resisting cement might not suffice to mitigate severe material degradation.

Keywords: Durability, External Sulphate Attack, Accelerators, Sprayed Materials, Sulphate-Resisting Cement.

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1. Introduction

Recent developments in set accelerators and spraying equipment have prompted the use of sprayed mixes with Portland cement in underground and other ground contention applications. The construction process consists of spraying a cementitious mix that consolidates upon reaching the substrate [1]. The mix must have adequate consistency and setting time to enable the build-up of layers with the desired thicknesses. Accelerators work to reduce the setting times and increase the early strength of the matrix, thus enabling the faster layer deposition and execution of challenging overhead elements. The accelerators also alter the matrix short- and long-term hydration, microstructure and properties [2–4].

Immediately after spraying, the material remains in direct contact with the surrounding soil and underground water, which may contain aggressive agents such as sulphates. As they penetrate through the interconnected porous network of the matrix, sulphates can react with aluminate phases in the matrix to form expansive compounds (secondary ettringite or secondary gypsum) and cause damage in a process known as external sulphate attack (ESA). Secondary ettringite formation in small pores (<50 nm) has been identified according to [5-6] as the main force to weakening the matrix due the cristallization in the pore. Other types can be adressed as gypsum secondary gypsum or thaumasite formation, aluminathe phases can react with Ca^{2+} or Na^{+} [6,7] To mitigate the consequences of the attack, most standards and recommendations rely on the specification of sulphate-resisting (SR) cements characterised by a limited C3A content (generally below 5% by cement weight [6-7]).

Nevertheless, this countermeasure only considers aluminates in the cement, falling short to account for the influence of aluminates coming from other sources, like the accelerators. It also does not account for the higher interconnected porosity induced by the spraying process and the very early exposure to sulphates that could favour the sulphate ingress and the ESA in comparison with conventionally cast matrices.

The lack of specific considerations might be a consequence of the limited knowledge about the impact of the spraying process with accelerators in the durability to ESA. To illustrate it, Table 1 summarises the variables and experimental methods from studies published in the last 20 years about the ESA in sprayed or cast mixes with and without accelerators.

Table 1. Recent studies about the ESA in matrices with Portland cement.

		References										This work
		[10]	[11]	[12]	[13]	[14]	[15]	[16]	[17]	[18]	[19]	
Variables	Before exposition (days)	57	57	15	14	14	14	57	28	-	7	7 and 28
	Type of mix	Cast	•		•	•	•	•	•	•	•	•
		Spray	•	•								•
	Cement	I	•	•	•							•
		II		•	•			•	•	•		•
		SR ^a	✗	✗	✓	✓	✗	✗	✓	✗	✓	✓
	Accelerators ^b	AF	•	•								•
		AR	•	•								•
	Dimension stability	•	•					•	•	•	•	•
	Velocity of US											•
Methods	Phase composition	•	•	•		•		•	•	•	•	•
	SEM	•	•	•		•		•		•		•
	Mechanical tests			•				•		•		•

a: sulphate-resisting according to [8,9]

b: alkali-free(AF) or alkaline (AR)

Notice that only [7] and [8] evaluate the influence of accelerators on the durability of sprayed mixes exposed to sulphates. Their findings suggest a link between the accelerators and the increase in the degradation induced by the ESA. However, none of these studies evaluates the impact of the age of exposition to the sulphates, assuming a time that might not represent real applications. More importantly, they do not assess the performance of mixes with SR cement,

which is essential to elucidate if the recommendation found in codes to mitigate the ESA also suffice for sprayed mixes with the accelerator. This critical gap in knowledge has potentially negative practical repercussions.

The objective of this work is to evaluate how the chemical composition of accelerators and the age of exposition to sulphates affect the degradation mechanism of sprayed mixes with SR cements subjected to ESA. In total, 8 mortar compositions were sprayed in laboratory conditions with 2 SR cement and 4 set accelerators. Cores and prisms were extracted and exposed to a sulphate solution at 7 and 28 days since production for 400 days. Evolution of phases, microstructure and macroscopic behaviour were characterized.

Results complement the limited literature on the behaviour sprayed mixes with accelerator subjected to ESA. Moreover, findings shed light on understanding the ESA consequences in sprayed mixes with SR cement at micro- and macro-structural levels depending on the accelerator type. Observations derived here might guide the selection of materials to enhance the durability of sprayed structures and help steer the definition of more appropriate recommendations in standards to mitigate the ESA in such application.

2. Experimental Program

2.1.

Materials

Mortar mixes contained either Cement I 52.5R (CEM I) or Cement II/A-L 42.5 R (CEM II) with 11.3% of limestone filler by cement weight (bcw). The former is employed in sprayed mixes in Asia and America [2,3], whereas the latter is widely used in Europe. Table 2 summarises the phase and chemical compositions of the cement determined by quantitative XRD and XRF spectrometry, respectively. Both cements comply with the requirements described in [20] and are SR according to [8,9].

A limestone aggregate (>99 % CaCO_3) with a particle density of 2.32 g/cm^3 , water absorption of 5.46% was used. The particle size distribution of the aggregate ranges from 0 mm to 1.25 mm, which is limited by the spraying equipment used in the experimental programme. Distilled water and a superplasticiser based on a polycarboxylate solution (34% solid content) were employed.

To represent the typical types in tunnelling applications, 2 alkali-free accelerators (AF060 and AF040), named because of the $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ molar ratio and based on aqueous solutions of aluminium sulphate and 2 alkaline accelerators (AR130 and AR080) named because of the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ molar ratio and based on aqueous solutions of sodium aluminate were chosen. Table 3 shows the main characteristics of these accelerators according to the supplier.

Table 2. Phase and chemical compositions of cement.

Phase Composition (%)			Chemical Composition (%)		
	CEM I	CEM II		CEM I	CEM II
C_3S	58.3	51.7	CaO	62.6	62.5
C_2S	11.2	6.7	SiO_2	19.9	17.6
C_4AF	13.4	14.8	Al_2O_3	4.7	4.0
C_3A_c	4.1	2.9	Fe_2O_3	3.3	3.5
C_3A_o	0.6	0.7	SO_3	3.5	3.2
CaO	1.1	1.2	MgO	1.9	1.7
Ca(OH)_2	1.7	0.7	K_2O	1.0	0.8
CaCO_3	1.9	11.3	TiO_2	0.2	0.2
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.1	0.7	P_2O_5	0.1	0.1
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	4.4	5.3	LOI	2.9	6.4
K_2SO_4	-	0.5			
$\text{K}_2 \cdot \text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$	1.1	-			
MgO	-	0.6			
MgCO_3	-	3.1			
Total	100.0	100.0	Total	100.0	100.0

Table 3. Characteristics of accelerators.

Characteristic	AF060	AF040	AR130	AR080
Solid content	48.0	68.5	43.0	61.9
Al_2O_3 content (%)	13.5	12.0	24.0	16.5
SO_4^{2-} content (%)	21.0	29.0	-	-
Na_2O content (%)	-	-	19.0	19.5

pH at 20°C	3.1	2.2	12.0	12.5
Al ₂ O ₃ / SO ₄ ²⁻ molar ratio	0.6	0.4	-	-
Al ₂ O ₃ / Na ₂ O molar ratio	-	-	1.3	0.8

Composition and preparation of mortars

Since the size of the aggregate does not play a key role in the chemical processes involved in the ESA, results obtained here might be taken as a reference of the trend expected for sprayed concrete and mortar [11]. The mixes were produced and tested at the Laboratory of Structures Luis Agulló at Polytechnic University of Catalonia and the Technological Center from the University of Barcelona (CCIT-UB).

Each batch served the production of specimens for all tests of each composition. The batches had 30 kg of cement, an aggregate/cement ratio equal to 1.7 by weight, water/cement (w/c) ratio equal to 0.51 by weight and 1.0 % of superplasticiser bcw. The following contents of accelerator bcw were determined according to [2] to represent the range typically found in tunnels executed with sprayed materials: 5% and 7% for AF060, 5% for AF040, 3% for AR130 and 3% for AR080.

Table 4 presents the chemical composition of each mix and their corresponding nomenclature that includes the Cement type (CI or CII), accelerator type (REF, AF060, AF040, AR130 and AR080), accelerator dosage in percentage and age of exposition (7 or 28 days), in this order and separated by “_”. The final C3A/SO₃ molar ratio of the mixtures were calculated by considering the total amount of sulfate remaining after the accelerator reaction. According to equation 1 (units in mol), sulfate remaining after accelerator addition (SO₄²⁻ left) corresponds to the sum of the sulfate contents in the cement (SO₄²⁻ in cement) and in the accelerator (SO₄²⁻ in accelerator) minus the sulfate consumed by the aluminium from the accelerator to form ettringite (SO₄²⁻ consumed by AFt formation).

$$\text{Final } \frac{C_3A}{SO_3} = \frac{C_3A_{\text{cement}}}{SO_4^{-2}{}_{\text{cement}} + SO_4^{-2}{}_{\text{accelerator}} - SO_4^{-2}{}_{\text{consumed by accelerator}}} \quad (\text{Eq 1})$$

The mixing process was performed in a planetary mixer type 65/2 K-3 with 150 and 40 rpm paddle and planetary rotations, respectively. First, all the cement and 90% of the water were mixed for 240 s. Then, the superplasticizer was added with the remaining water and homogenized for 240 s. Finally, the aggregate was added and mixed for 300 s. After the mixing process, mortars were kept for 1 h at 20 °C until the spraying process. This procedure, also adopted by [3,21,22], intends to reproduce the typical field conditions as concrete must be transported from the batching plant to the jobsite before spraying takes place.

Table 4. *Chemical composition of sprayed mortars.*

Name	Composition (mmol /g _{cement})						
	Total SO ₄ ⁻² in cement	Al in accele. ^a	SO ₄ ⁻² in acceler.	AFt formed ^b	SO ₄ ⁻² consumed by AFt formation ^c	SO ₄ ⁻² left	Final C ₃ A/SO ₃
CI_REF ^(d)	0,44	-	-	-	-	0,44	0.59
CI_AF060_5%	0.44	0.13	0.11	0.07	0.20	0.35	0.73
CI_AF040_5%	0.44	0.12	0.15	0.06	0.18	0.26	0.63
CI_AR130_3%	0.44	0.14	-	0.07	0.21	0.23	1.13
CI_AR080_3%	0.44	0.10	-	0.05	0.15	0.29	0.90
CII_REF ^(d)	0.40	-	-	-	-	0.40	0.44
CII_AF060_5%	0.40	0.13	0.11	0.07	0.20	0.31	0.56
CII_AR080_3%	0.40	0.10	-	0.05	0.15	0.25	0.70

^a Al corresponds to Al³⁺ and [Al(OH)₄]⁻ in alkali-free and alkaline accelerators, respectively.

^b AFt phase formed by the accelerator.

^c Corresponds to the SO₄⁻² consum during the formation of the Aft phase.

^d Not sprayed.

Spraying process

The wet-mix spraying process is the most commonly used in underground construction around the world [2] and was selected for this experimental programme. The spraying

happened inside a climatic chamber at 20 °C and 90% relative humidity. The mortar was sprayed in metallic panels forming a 45° angle with the horizontal plane and placed inside the climatic chamber shown in Figure 1.a. The dimensions (see Figure 1.b) and spraying of the panels were based on [23].

The equipment used to spray the mortars in the laboratory (see Figure 1.c) is a small-scale version of the setup found in previous research [2] and underground construction with concrete. The mortar was pumped by the UP-Pictor screw pump (Fig.1.c item #1) operating at 6 bar of pressure provided by 3 HP air compressor. The screw pump was chosen for its constant flow and absence of pulsation effect.

Figure 1. (a) Arrangement of panels inside the climatic chamber, (b) dimensions of the metallic panels, (c) spraying equipment in laboratory conditions and (d) spray gun.

The material moved through the hose (Fig.1.c item #2) and entered the spray gun (Fig.1.c item #3) through the main entrance (Fig 1.d item #7). Compressed air (Fig 1.d item #8) and accelerators (Fig 1.d item #9) were pre-mixed in a small chamber within the spray gun (Figure 1.d item #10) and, then, homogenised with the mortar inside the nozzle (Figure 1.d item #11). The resulting mix exited the nozzle at high speed and was sprayed onto the metallic panels.

The accelerators (Fig.1.c item #4) were dosed by an air-operated diaphragm pump (Fig1.c. item #5) connected to the compressor (Fig.1.c item #6). This type of pump provided a homogeneous suction for all accelerators tested, regardless of the differences in their viscosity. The flow of accelerators was calculated based on the optimal flow of mortar (5.0 L/min). Once the spraying process ended, the remaining unsprayed mortar was poured in metallic moulds placed horizontally over the ground to produce the reference cast specimens (without spraying and accelerator).

187

188 **Specimen preparation.**

189

190 All panels remained in the moulds for 24 h, when they were demoulded and placed in a humid
191^{2.4.} chamber (20 °C and 99% relative humidity) for 24 h more. Once the mortar reached enough
192 strength (48 h after production), prismatic and cylindric specimens were extracted and prepared
193 for the tests. Prismatic specimens were saw cut to the dimension 25x25x250 mm based on the
194 ASTM C490 [24] for assessing the dimensional variation in mortar specimens. Cylindric
195 specimens were drilled using core bits with approximately 25 mm diameter and cut to a length
196 of 25 mm following the methodology in [23] to ensure the slenderness ratio of 2 [23]. **Regions**
197 **at the inclined edges of the panel and near the mould and outer surfaces were discarded as they**
198 **are prone to lamination.**

199

200 **Specimens that did not present regularity (± 1 mm), parallelism and proper dimensions ($\pm 1\%$)**
201 **after the cutting process were discarded. When this analysis was finished and specimens**
202 **were selected, they were cleaned with compressed air and water to avoid the presence of**
203 **dust. As ESA is a diffusion process, this was carried out to avoid the saturation of the external**
204 **pores of the specimens and the cores.**

205^{2.5.}

206 **Exposure conditions**

207

208 After the extraction, specimens were submerged in water at 20 °C until the start of sulphate
209 exposure at 7 or 28 days since production, when they were submerged in a sodium sulphate
210 solution with a concentration of 30 g/L and 20 °C. For comparison, reference samples of each
211 composition were submerged in water. The earliest exposure time (7 days) was defined to
212 allow enough time for the preparation of specimens, initial inspection and homogenisation of
213 their saturation degree. The pH of the solutions was measured every 7 days for the first three

months and once a month afterwards. The solutions with sulphates were renewed every month or if the pH was above 11.

Test Methods

Table 5 shows the tests performed with cylindrical and prismatic specimens, which include techniques for assessing the macro and microstructural characteristics during the ESA. The start of the exposure to sulphates was considered time 0 for the accelerated ESA tests and the analysis of the results.

An adaptation of the ASTM C490 [24] was used to evaluate the dimensional variation of prismatic specimens. A Digital Demec strain gage measured the change in the distance between 2 stainless steel pins glued 150 mm apart along the biggest size of the specimen. The measurements were taken weekly during the first month and every other week until the end of the test at 400 days. Before assessing the dimensional variation, specimens were subjected to a visual inspection - to identify cracking, change of colour and spalling - and ultrasound wave velocity test - to indirectly evaluate the matrix deterioration. The equipment Pundit PL-2000 with transducers operating at a frequency of 0.5 MHz in direct transmission was used to measure the ultrasound wave velocity (UWV). The transducers were always placed at the exact half of the specimen to minimise the variability of the results.

Table 5. Tests performed with cylindrical and prismatic specimens.

Test	Specimen	Number of replicas		Time (days)	Reference
		Sulphate solution	In Water		
Porosity	Cylindrical		3	Prior to sulphate exposure	[25]
Dimensional Variation	Prismatic	6	3	0 to 400	[24]
Visual inspection		6	3	0 to 400	-

Ultrasound Wave Velocity		6	3	0 to 400	[22]
Compressive Strength	Cylindrical	3	3	90	[26]
XRD	Prismatic	1 per age	-	20, 40,150,300	[3,27]
SEM		1 per age	-	400	[28]

To assess the evolution of phase composition over time, X-Ray powder diffraction (XRD) was performed in samples extracted from the prismatic specimens exposed to the sulphate solution. A 2 mm-wide slice was cut from the prismatic specimen at 20, 40, 150 and 300 days. These were crushed and ground to a maximum particle size of 63 μm . The powder obtained was analysed by XRD in a PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg-Brentano $\theta/2\theta$, using $\text{CuK}\alpha 1$ ($\lambda = 1.5406 \text{ \AA}$) radiation at 45 KV and 40 mA. The powder diagrams were analysed quantitatively by Rietveld refinement using the software X'Pert High Score Plus and the structure models in Table 6. To quantify the amorphous content of the samples, Rutile (99% pure) was added at 20% by sample weight as an internal standard.

Scanning electron microscopy (SEM) was used to analyse the microstructure of samples from the middle region of the prismatic specimen at the end of the attack. These were frozen in liquid nitrogen, vacuum dried during 24 h and coated with carbon. The morphology of phases was analysed in the fracture surfaces, and their chemical composition was assessed by energy dispersive X-ray analysis.

Table 6. Phase structures used in the Rietveld analysis.

Phase	Formula	Crystal System	PDF Codes	ICSD	Ref
Alite	Ca_3SiO_5	Monoclinic	01-070-8632	94742	[29]
Calcium Aluminate	$\text{Ca}_3\text{Al}_2\text{O}_6$	Cubic	00-038-1429	1841	[30]
Ferrite	$\text{Ca}_2\text{AlFeO}_5$	Orthorhombic	01-071-0667	9197	[31]
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Monoclinic	00-033-0311	151692	[32]
Calcite	CaCO_3	Rhombohedral	01-083-0577	79673	[33]
Portlandite	$\text{Ca}(\text{OH})_2$	Rhombohedral	01-072-0156	15741	[34]
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot (\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	Hexagonal	00-041-1451	155395	[35]
Monosulfoaluminate	$\text{Al}_2(\text{OH})_{12} \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$	Rhombohedral	--	24461	[36]

Hemicarboaluminate	$\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot \text{OH} \cdot 0.5\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Rhombohedral	00-041-0221	263124	[37]
Monocarboaluminate	$\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot (\text{CO}_3) \cdot 5\text{H}_2\text{O}$	Triclinic	01-087-0493	59327	[38]
Thenardite	Na_2SO_4	Orthorhombic	01-070-1541	2895	[39]
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Rhombohedral	01-075-1761	31335	[40]
Quartz	SiO_2	Hexagonal	01-083-2465	200721	[41]
Rutile	TiO_2	Tetragonal	01-089-4202	44881	[42]

3. Results and discussion.

Porosity characterization before sulphate exposure

Figure 2 depicts the results of water accessible porosity for all sprayed and poured mixes before immersion in the sulphate solution at 7 or 28 days since production. As expected, a reduction in porosity is observed from 7 to 28 days. Such variation is mainly attributed to the hydration of phases in the cement since the exposition to sulphates had not started yet.

Figure 2. Water accessible porosity.

On average, the porosity reduction in the reference compositions (not sprayed and without accelerators) is 2.7 times **higher** than in sprayed compositions with accelerators. This result confirms findings of previous studies [2,43] and **indicates** that the incorporation of accelerators **compromises** the proper consolidation of the sprayed material and the elimination of entrapped air due to the fast setting of the matrix. As described by [44], this may also be explained by the inhibition of alite hydration in accelerated mortars, which limits the amounts of hydration products formed and the filling of pores.

The results obtained are similar to previous publications [2,43]. They suggest that sprayed mixtures have the highest values of porosity at both ages due the incorporation of accelerators, which reduce the setting time of the matrix. Therefore, the matrix does not consolidate properly and does not eliminate the entrapped air, increasing its porosity. The

results are directly proportional to the ettringite formation calculated in Table 4, the exceptions are the mixtures with the AR080 accelerator.

Comparing the porosity of CI_AR080_3% (16.24%) and CI_AR130_3% (14.22%), the mixtures that incorporates AR080 presents the lowest ettringite formation and the lowest $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ ratio. One possible explanation is the incorporation of elevated concentrations of sodium, this may lead to a porous matrix [45,46] due to the variation in the composition and compactness of the C-S-H chains and the AFm phases.

In average the reduction in water accessible porosity from 7 to 28 days in the reference mixtures is 5.9 %, in the sprayed mixtures this value is 2.2 %. As alite hydration is inhibited in accelerated mortars [44], lower amounts of hydration products are formed. Because of that, the filling of pores occurs less intensively, leading to lower reductions in porosity.

3.2. Dimensional variation

Figure 3.a and 3.b show the dimensional variation over time for the specimens with CEM I and CEM II, respectively. The values presented in the graphs are the difference between the average dimensional variation for the composition submerged in the sodium sulphate solution and the average dimensional variation for the same composition submerged in water. This procedure intends to isolate the expansion attributed to the ESA from the expansion that could happen as a result of the hydration of phases in a submerged condition.

Figure 3. Dimensional variation in sprayed mortars with (a) CEM I and (b) CEM II.

The reference cast specimens (CI_REF_28 and CII_REF_28) present negligible dimensional variation caused by sulphate penetration over 400 days of ESA. Such results may be attributed to the low aluminate content of these cement that are considered SR [20] and to the

lower porosity of the mixes extracted from cast panels without accelerator. By contrast, the specimens of sprayed mortars with accelerator show expansions ranging from 0.5 to 7 mm/m at 400 days. This may be the result of the higher porosity induced by the spraying process, which could favour sulphate ingress and the additional aluminate content provided by the accelerators that could contribute to the formation of expansive phases.

The mixes with AR accelerators show more significant expansion than the mixes produced with AF accelerators. Notice that specimens sprayed with AR accelerators present the highest porosity (Figure 2) amongst all analysed here. The significant expansion of the mix with AR080 accelerator is enough to produce an early failure of the specimens and the interruption of the test. Specimens with AR080 accelerator using CEM I and CEM II exposed to sulphates at 28 days since production failed approximately 120 days after the beginning of accelerated ESA. Specimens with AR accelerator and CEM II exposed to sulphates at 7 days since production withstood even less time in the accelerated ESA, failing only 30 days from the beginning of the test. This suggests that the spraying process with accelerates leads to a significant reduction in the expected durability in comparison with reference cast specimens without accelerators. Such reduction is observed despite using SR cement and is particularly evident in mixes with AR accelerators.

Specimens exposed to sulphates at 7 days since production presented up to 5-times higher expansion than equivalent specimens exposed to sulphates at 28 days since production. These differences appear faster in mixes with AR accelerator than in mixes with AF accelerator. Both outcomes may be related to the more rapid sulphate ingress induced by the larger interconnected porosity at 7 days in comparison with 28 days and in mixes with AR accelerator in comparison with those with AF accelerators.

Skalny et al. [47] suggest an expansion of 0.1% as a safe margin for determining the maximum expansion without significant degradation in mixes under sulphate attack.

Crammond [48] recommends that the 0.1% expansion should not be exceeded after 6 months of testing. Although the experimental procedure adopted may affect the results, only cast specimens without accelerators fulfil this requirement, which is consistent with the use of SR cement. Conversely and despite using the same cement, 5 of the mixes sprayed with accelerator show expansions between 2.1 and 8.7 times higher than the limit while the remaining 3 had already failed much before reaching 6 months of testing.

Visual Inspection

3.3.

Figure 4 shows images from the visual inspection of specimens at the beginning of the ESA and at the latest time during the test (400 days for those not failing and less for those failing before the end of the test). All cast specimens experience a slight change in their surface colour during the 400 days of sulphate exposure, which may be related to the precipitation of phases (see example in Figures 4.a and 4.b for CI_REF_28 and CII_REF_28, respectively). By contrast, in addition to the change in colour, almost all sprayed specimens with accelerator present cracking, as shown in Figures 4.c to 4.j. This confirms that the spraying process with accelerators might reduce the durability in elements exposed to ESA.

Figure 4. Visual inspection of the cast and sprayed specimens before and after the accelerated ESA.

The mixes with the accelerator AR080 present the highest degrees of degradation (Fig 4.f, Fig 4.i and Fig 4.j), with longitudinal and transversal cracking near the edges and in the central part of the specimens. These results are consistent with the higher expansion measured in sprayed mixes with AR accelerator.

Edge cracking is usually the first visual consequence of the ESA, associated with an intensification of sulphate penetration combined with low material confinement in those

regions. Longitudinal and cracking of the cross section are serious failure modes caused by the interaction between the sound core of the specimen and the external layers directly affected by sulphate penetration. Figure 4 shows that failure in the cross-section happens more often than longitudinal cracking or spalling, which agrees with the findings by [49,50]. These authors stated that the tensile stress generated in the core of specimens with small cross-section due to the expansion of the external layers (related to cross-sectional failure) are more critical than the stress generated in the interface between the damaged and sound regions (related to spalling).

Specimens exposed to sulphates at 7 days show earlier formation of cracks and higher degrees of damage than specimens exposed to sulphates at 28 days. The comparison of specimens with different cement types (Figure 4.a and 4.b or Figure 4.f and 4.i) does not reveal any significant difference, thus suggesting a similar behaviour.

4.4. Ultrasound wave velocity (UWV).

Figure 5 presents the evolution of the UWV over time for mixes subjected to ESA. Variations in the UWV are caused by changes in the density, elastic modulus and integrity of the specimens. All curves in Figure 5 show a similar trend characterised by two stages: an increase of the UWV up to a maximum (Stage 1) followed by a reduction of UWV until the end of the test or failure of the specimen (Stage 2).

Stage 1 comprises the early ages of the attack when the phases produced by cement hydration and the ESA contribute to reduce the porosity and the ESA contribute to reduce the porosity and increase the mechanical properties of the mixture caused by the space filling. This effect caused by the precipitation prevails. In Stage 2 - comprehending from maximum UWV onwards - the deposition of expansive phases causes significant micro-cracking that acts like

obstacles to the wave propagation. This effect prevails over the potential increase arising from the densification of the matrix.

Figure 5. UWV in mixes subjected to ESA.

Table 7 summarises the initial UWV at the start of the exposure to ESA (UWV_0), the variation observed during the test ($UWV_{end} - UWV_0$), the maximum velocity (UWV_{max}) and the time it occurs (t_{max}), and the maximum variation ($UWV_{end} - UWV_{max}$). Notice that UWV_{end} refers to the last measurement taken (at 400 days for specimens not failing and at time of failure for others).

From time 0 to the end of the test, cast mixes experience a UWV increase consistent with limited micro-structural damage due to the ESA. Conversely, sprayed mixes with accelerators present mainly negative UWV variations, which indicate significant micro-structural deterioration.

Table 7. Parameters obtained from the UWV curves in Figure 5.

Mortar Sample	UWV_0 (m/s)	UWV_{max} (m/s)	t_{max} (days)	$UWV_{end} - UWV_{max}$ (m/s)	$UWV_{end} - UWV_0$ (m/s)
CI_REF_28	4055.6	4158.9	126	-46.1	57.2
CI_AF060_5%_7	3881.9	4115.1	56	-230.2	3.0
CI_AF060_5%_28	3938.5	4107.1	56	-146.0	22.6
CI_AF040_5%_28	3946.9	4104.7	21	-163.5	-5.7
CI_AR130_3%_7	3826.3	4007.4	42	-474.8	-293.8
CI_AR130_3%_28	3872.8	4107.8	28	-454.2	-219.2
CI_AR080_3%_28	3697.0	3887.8	28	-438.7	-247.9
CII_REF_28	3980.5	4062.7	126	-50.8	31.4
CII_AR080_3%_7	3318.6	3471.4	21	-797.2	-644.4
CII_AR080_3%_28	3651.5	3753.7	21	-338.8	-236.6

UWV_{max} occurs 2.3 to 6.0 times earlier in sprayed mixes with accelerator than in cast mixes without accelerator. This reveals a quicker onset of the damage, possibly due to a more rapid

410 sulphate ingress promoted by the higher porosity and the capacity to form expansive phases in
411 sprayed mixes with accelerators. After reaching UWV_{max} , cast mixes experience a UWV
412 reduction 14 times smaller than that observed in sprayed mixes with accelerators, which
413 confirms the more intense damage of the latter due to the ESA.

414
415 The level of degradation assessed for mixes with AR accelerators is on average 2.5 times
416 higher than that of mixes with AF accelerators. Such results are consistent with the visual
417 inspection and the dimensional variation in Figure 3. Mixes with Al_2O_3/Na_2O ratio of 0.8
418 (AR080) present a higher deterioration in a shorter period than the mixes with Al_2O_3/Na_2O
419 ratio of 1.3 (AR130). This suggests that a lower Al_2O_3/Na_2O ratio may affect negatively the
420 durability of accelerated matrices exposed to sulphates. The higher proportion of sodium in
421 relation to aluminates could contribute to the formation of AFm with higher solubility that
422 would react and form ettringite more quickly.

423 424 4.5. Compressive strength

425
426 Table 8 shows the average compressive strength ($\bar{X}$) at 98 days for the mixes with CEM I and
427 the relative reduction between the mixes exposed to sulphate and equivalent ones in water.

428 All compositions exposed to sulphates show a strength reduction due to the progressive
429 micro-cracking associated with the ESA. The mix CI_REF_28 presents the smallest relative
430 reduction, which reflects the limited damage expected in cast mixes with SR cement.

431
432 Relative reductions are marginally higher in sprayed mixes with AF accelerators for the first
433 98 days of exposition to sulphates, which suggests that the additional damage observed in the
434 UWV and dimensional variation caused by the ESA does not significantly compromise the
435 compressive strength. Conversely, sprayed mixes with AR accelerator showed relative
436 differences 6.6 to 9.6 times higher than those of cast specimens and overall compressive

strength reductions of up to 46.24%. The results confirm that the accelerator type influences significantly the compressive strength during the first 98 days of the accelerated ESA.

Table 8. Compressive strength for mortars with CEM I.

Mix	In water		In Na ₂ SO ₄ solution		Relative reduction (%)
	$\bar{X}$ (MPa)	CV (%)	$\bar{X}$ (MPa)	CV (%)	
CI_REF_28	38.66	5.48	36.80	11.38	4.83
CI_AF060_5%_7	31.48	26.04	29.15	21.04	7.38
CI_AF060_5%_28	33.32	19.78	31.19	24.07	6.40
CI_AR130_3%_7	31.57	12.96	16.98	23.06	46.24
CI_AR130_3%_28	34.70	23.93	23.69	19.74	31.72

Sprayed mixes with AF and AR accelerators exposed at 7 days since production present respectively 13.3% and 31.4% higher relative strength reduction in comparison to corresponding ones exposed at 28 days since production. In other words, the sprayed mix with AR accelerator is 2.2 times more sensitive to the age of exposition than equivalent sprayed mix with AF accelerator. The trends observed here are consistent with those identified in previous tests.

3.6.

X-ray diffraction

Figure 6 shows the mass percentage of ettringite (6.a) and gypsum (6.b) formed during the exposition to sulphates. The quantification of AFm was deemed not accurate enough due to the low intensity of the AFm peaks compared to the intensity of calcite peaks from the aggregate (>60% of the composition by weight). Assessment for mixes whose specimens failed before the end of the test were only conducted until the damage led to a free sulphate ingress in the matrix, thus potentially compromising the quantification. The missing results for later times are represented in red with the same magnitude as the last valid quantification.

The amount of ettringite in mixes without accelerator (CI_REF_28 and CII_REF_28) is significantly smaller than in the rest of sprayed mixes throughout the accelerated test. Since accelerators provide an extra source of aluminium to the mortar, a larger amount of AFm phase is expected as hydration progresses [3,21]. Therefore, more ettringite should be quantified in accelerated matrices as AFm phases react with the sulphate ions from the solution, forming secondary ettringite. The secondary ettringite formed is the main responsible for the expansion in Figure 3 and the degradation found in visual inspections, UWV and compressive strength.

Figure 6. Phases formed in the mixes: (a) Ettringite and (b) Gypsum.

The amount of gypsum (Fig 6.b) is lower than 1% in all mixes except for the ones with AR080 accelerator. The formation of gypsum can be a preliminary stage to the formation of ettringite. However, as mentioned by [20], it is still unknown if the gypsum intervenes in the expansions and deterioration caused by the ESA.

The formation of secondary ettringite is also influenced by the accelerator type. Mortars containing AR accelerators (CI_AR130_3%_28 and CI_AR080_3%_28) present larger amounts of ettringite compared to the equivalent mortars produced with AF accelerators (CI_AF060_5%_28 and CI_AF040_5%_28) at 300 days of ESA. Since the AR accelerators has a higher C_3A/SO_3 ratio, larger amounts of AFm phases are formed, leading to a higher quantity of secondary ettringite during the ESA.

The higher amount of ettringite in mortars containing AR accelerators is also influenced by the addition of sodium to the mix. The AFm formed in the presence of high sodium concentration is in a U-phase [21,27]. The U-phase is a mineral observed for first time by Dosch and zur Strassen [51]. In their study they found that a new phase was formed and the plausible composition was established as $4CaO \cdot 0.9Al_2O_3 \cdot 1.1SO_3 \cdot 0.5Na_2O \cdot 16H_2O$, and it

belongs to the group of hexagonal or pseudo-hexagonal layered structures like the AFm, where sodium is present between the layers increasing the interlayer distance of the crystals [52].

The cast mixes with CEM I present higher content of ettringite than equivalent mixes with CEM II. This is consistent with the higher C_3A content in the CEM I (4.7% bcw) in comparison with CEM II (3.6% bcw), which should be proportional to the potential to form ettringite. The same trend is not as clear in sprayed mixes due to the interaction with compounds provided by the accelerators and the early damage experienced by specimens.

Results at 300 days reveal that mixes exposed to sulphates at 7 days since production have approximately 1.33 times more ettringite than equivalent mixes exposed to sulphates at 28 days since production. The larger ettringite content is also related to the higher connected porosity of mixes exposed at earlier ages, which favours the sulphate ingress and the consequent formation of ettringite. As hydration progresses, the porosity is reduced, limiting the diffusion of sulphates in the matrix. The influence of this variable is particularly evident in mixes with AR080 accelerator whose specimens exposed at 7 days since production have twice as much ettringite as specimens exposed at 28 days. This is possibly one of the reasons for the earlier failure of specimens exposed to sulphates at 7 days in comparison with those exposed at 28 days since production.

3.7.

Scanning Electron Microscopy

Mortar compositions CI_REF_28, CI_AF060_3%_28, CI_AR130_3%_28 and CI_AR080_3%_28 exposed to sulphates were evaluated through SEM at 400 days. Figure 7 shows the results for the cast mix CI_REF_28 without accelerator. The regions analysed by EDS are indicated by a white circle in the image. Results obtained in the EDS spectra are

represented as the relative intensities of each element, placed above each image. These intensities are important to identify the relative relation between each other and correlate with the chemical composition of the phases analyzed. The peaks considered to measure the intensity of Ca, Si, S and Al correspond to the energies of 3.73, 1.78, 2.33 and 1.52 keV, respectively. The intensity-base ratios are important to identify the presence of the hydrated aluminium phases. According to [21,44], a 0.33 ratio indicates the presence of ettringite. Ratios below 0.33 indicate the presence of ettringite and sulfates. Normally, the ultimate phase of the aluminium hydration is monosulfoaluminate ($Al/S = 0.66$) and C-A-H hydrates ($Al/S \geq 0.66$). Al/S ratio values between 0.33 and 0.66 indicate the possible presence of a secondary product like ettringite in the pores [3,21,44].

Figure 7. SEM images and EDS analysis of pore (a) and detail of ettringite formation (b) in CI_REF_28.

Figure 7.a shows a pore filled with plate-like crystals. The Al/Ca, Si/Ca, and Al/S intensity-base ratios are respectively equal to 0.24, 0.16 and 0.72, indicating a potential presence of C-S-H, AFt and AFm phases. Further approximation inside the pore reveals needle-like crystals measuring 10 μm in length characterised by an Al/S intensity-base ratio of 0.63, indicating the presence of ettringite (see Figure 7.b). Ettringite in this case seems to appear with the AFm phase ($Al/S \geq 0.66$) indicating that secondary ettringite is barely formed due to the low C_3A content in the cement. Normally, it is expected to find ettringite in earlier stages of hydration. However, these samples are 400 days old. The presence of AFm is expected in higher ratios as is the normal hydration of aluminates in cement. The results are in line with the low ettringite formation detected in XRD analyses of the mix (see Figure 6). Sodium was not identified in the EDS of the sample.

Figure 8 shows the SEM images and the EDS of the sprayed mix CI_AF060_5%_28. The EDS spectrum In Figure 8.a shows Al/Ca, Si/Ca and Al/S intensity-base ratios respective equal to 0.11, 0.19 and 1.1, indicating presence of C-S-H and AFm phases. The main sulfoaluminate phase found was AFm, which can be related to the introduction of sulphates ions by the accelerator.

Figure 8. SEM image and EDS analysis of the matrix (a) and ettringite formation (b) in CI_AF060_5%_28

Figure 8.b shows a pore filled with 20 µm-long needle-like formation with an Al/S intensity-base ratio of 0.30, indicating a combination of AFt phase and sulphates. This is consistent with the XRD results that show increasing contents of ettringite in mixes with AF accelerator in comparison with those without accelerator. Once more, sodium was not found in the matrix or the pores.

Figure 9 shows SEM images and the EDS analysis of the mix CI_AR130_3%_28. Figure 9.a reveal Al/Ca, Si/Ca and Al/S intensity-base ratios that suggest the presence of ettringite and C-S-H. In this case, sodium is found in EDS results of the sample. The sodium could come from the alkaline accelerator and the Na₂SO₄ diluted in water. Since the sodium was only found in the mixes with the AR accelerator, the most likely source is deemed the accelerator that incorporates Na⁺ and Al[(OH)₄]⁻ ions into the matrix during hydration [3]. Depending on the Na⁺ concentration, phases with sodium, calcium and aluminate may be formed.

Figure 9. SEM image and EDS analysis of the matrix (a) and ettringite (b) in CI_AR130_3%_28

The presence of sodium may lead to a more porous matrix [45,46] due to variation in the composition of C-S-H and AFm phases. In Figure 9.a, sodium is found in the C-S-H

composition, which changes to a system with lower density due to the lower Ca-Si/ (Si+Al) ratio compared to alkali-free systems [45,46]. AFm phases were not found in Figure 9, probably due to the enhanced solubility of these phases in the presence of sodium. Figure 9.b shows the inside of a pore characterised by an Al/S ratio equal to 0.46 that is consistent with ettringite in the presence of sulphates.

Figure 10 shows the SEM images and the EDS of the mix CI_AR080_3%_28. According to the EDS results in Fig 10.a, Al/Ca, Si/Ca, and Al/S **intensity-base** ratios respectively of 0.07, 0.15 and 0.38 indicate a possible presence of C-S-H and AFt phases. Sodium is also found with a Na/Ca **intensity-base** ratio equal to 0.23, which is **higher** than in the mix with AR130 (0.07). Sodium seems to remain in the C-S-H, which explains the **higher** porosity found in the mixes with accelerator AR080. Figure 10.b shows the formation of 40 µm-long needle-shaped crystals with Al/S **intensity-base** ratio equal to 0.22, indicating a typical ettringite formation with a high content of sulphates. These are the longest and more abundant ettringite needles found across all specimens analysed, thus justifying the XRD results and the damage observed in sprayed mixes with AR080.

Figure 10. SEM image and EDS analysis of (a) detail of the C-S-H and (b) Ettringite formation in CI_AR080_3%_28.

4. Influence of theoretical C_3A/SO_3 of the mix with accelerator

Figure 11 shows the relationship between the theoretical C_3A/SO_3 of the mix with accelerator summarised in Table 4 (x-axis of all graphs) and the main results obtained in the experimental programme (y-axis). Only results of mixes exposed to sulphates 28 days since production are depicted in Figure 11 to ensure the comparison under nearly identical conditions. The reduction of compressive strength and porosity were assessed at 90 days of sulphate exposure

and just before sulphate exposure, respectively. Other results correspond to approximately 300 days of accelerated ESA.

Figure 11. Relationship between the theoretical C_3A/SO_3 of the mix with accelerator and the ettringite formation, maximum ultrasound variation, linear expansion, strength reduction and porosity

A similar linear trend is observed for the ettringite formation, the maximum ultrasound variation, the linear expansion and the reduction of compressive strength (notice that results for only 3 mixes are available for the latter). This confirms that the increase of the theoretical C_3A/SO_3 of the mix with the accelerator is related to the potential ettringite formation and the consequent magnitude of micro- and macro-structural changes induced by the ESA. A less clear trend was observed with the porosity, which is influenced by other aspects related to the production process that might have eclipsed the effect of the C_3A/SO_3 .

5. Conclusions

The following conclusions are derived from the study conducted here.

- Sprayed mixes with accelerator showed more ettringite, larger ettringite crystals and several times larger linear expansion than equivalent cast mixes without accelerator. This led to more damage at the micro- and macro-structural levels observed in the ultrasound results, visual inspection and mechanical tests results. The spraying process increases the interconnected porosity and favours the sulphate ingress. The inclusion of set accelerators provides an additional amount of aluminate phases that may react with sulphates in the ESA and contribute to the development of expansion and damages. Both factors seem the main responsible for the higher vulnerability to the ESA of sprayed mixes with accelerator in comparison with equivalent cast mixes without accelerator. A direct relationship was found

between the theoretical C_3A/SO_3 of the mix with accelerator and the expansion- and damage-related parameters assessed during the ESA.

- Alkaline accelerators triggered higher ettringite formation, expansion and deterioration than alkali-free accelerators. The absence of sulphates in alkaline accelerators leads to larger amounts of AFm phases (main source of secondary ettringite). Notice that ettringite was consistently found within the gel in sprayed mixes with alkaline accelerators tested here. Expansive products formed at these locations are more likely to generate damage due to the low capacity of the gel to accommodate the expansions

- The results suggest that the age of sulphate exposure plays a major role in the durability of sprayed specimens to the ESA. Specimens exposed at 7 days since production had significantly higher deterioration and expansion than those exposed at 28 days since production. As most sprayed structures are exposed to sulphates immediately after spraying, the accelerated ESA on specimens should be performed at earlier ages to obtain more realistic predictions for such applications.

- Despite using SR cement in all mixes, sprayed specimens presented severe and early signs of damage, which was not found in any of the reference cast specimens without accelerator. While both cast mixes without accelerator experienced expansion below the limit considered safe according to the literature [47][48], mixes sprayed with accelerator showed expansions more than 2.1 times the limit or failed even before the 6 months of testing. This reveals that the use of SR cement in sprayed mixes with accelerators is not enough measure to mitigate the consequences of the ESA.

Based on these findings, the following practical recommendations are proposed to reduce the negative consequences of ESA in elements exposed to sulphates and constructed with sprayed mixes with accelerators.

- The common practice found in guidelines and adopted in projects that rely mainly on the use of SR cement should be revisited. Limitations should be defined for the total content of potentially expansive aluminates (cement+accelerator) per volume of concrete and the C_3A/SO_3 .

- In the absence of such recommendations, specific experimental tests should be conducted to assess the impact of spraying with accelerators on the durability of mixes subjected to ESA.

- Alkali-free accelerators should be the preferred choice in applications under risk of ESA. If alkali-rich accelerators must be used, those with lower sodium content should be chosen.

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807 Appendix A. Appendix

808 Results of length variation of all the mixtures obtained by periodic measures are shown from
809 Tables A.1 to A.3. Tables A.1 to A.3 show the length variation (x 10⁻³) result from extracting
810 length variation of the specimens submerged in water.

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815 Table A.1 Length Variation (x 10⁻³) of the mixtures from 0 to 98 days.
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Mixtures	Time(days)									
	0	7	14	21	28	42	56	70	84	98
CI_REF_7	0	-0.021	0.019	0.033	-0.006	-0.017	-0.078	-0.082	-0.090	-0.077
CI_REF_28	0	-0.002	-0.007	-0.016	-0.041	-0.045	-0.050	-0.054	-0.047	-0.031
CI_AF060_5%_7	0	0.101	0.121	0.131	0.163	0.226	0.254	0.292	0.275	0.292
CI_AF060_5%_28	0	0.016	0.042	0.083	0.108	0.121	0.130	0.233	0.260	0.280
CI_AF040_5%_28	0	0.042	0.055	0.061	0.080	0.085	0.057	0.056	0.052	0.100
CI_AR130_3%_7	0	0.182	0.201	0.254	0.219	0.241	0.253	0.283	0.284	0.282
CI_AR130_3%_28	0	0.034	0.036	0.052	0.079	0.090	0.126	0.099	0.085	0.096
CI_AR080_3%_28	0	0.081	0.148	0.195	0.221	0.396	0.923	1.534	2.137	3.738
CII_AR080_3%_7	0	0.153	0.232	0.736	2.144	7.846	—	—	—	—
CII_AR080_3%_28	0	0.069	0.126	0.155	0.228	0.585	0.613	0.757	0.800	1.127
CII_REF_7	0	0.065	0.140	0.138	0.107	0.182	0.158	0.127	0.119	0.109
CII_REF_28	0	-0.032	-0.002	-0.005	-0.041	-0.028	-0.081	-0.064	-0.063	-0.056

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818 Table A.2 Length Variation (x 10⁻³) of the mixtures from 112 to 294 days.
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Mixtures	Time (days)									
	112	126	140	154	168	182	210	238	266	294
CI_REF_7	-0.035	-0.082	-0.057	-0.071	-0.067	-0.071	-0.109	-0.133	-0.088	-0.052
CI_REF_28	-0.036	-0.040	-0.058	-0.043	-0.045	-0.073	-0.104	-0.107	-0.055	-0.056
CI_AF060_5%_7	0.330	0.379	0.457	0.544	0.612	0.698	0.834	1.071	1.314	1.507
CI_AF060_5%_28	0.314	0.293	0.307	0.310	0.301	0.291	0.312	0.334	0.334	0.355
CI_AF040_5%_28	0.134	0.152	0.173	0.191	0.201	0.213	0.242	0.259	0.357	0.435
CI_AR130_3%_7	0.289	0.310	0.341	0.522	0.667	0.872	0.978	1.294	1.726	2.180
CI_AR130_3%_28	0.151	0.167	0.171	0.171	0.217	0.217	0.333	0.413	0.607	0.881
CI_AR080_3%_28	6.001	7.101	-	-	-	-	-	-	-	-
CII_AR080_3%_7	-	-	-	-	-	-	-	-	-	-
CII_AR080_3%_28	1.541	2.082	2.704	3.380	-	-	-	-	-	-
CII_REF_7	0.157	0.200	0.211	0.236	0.170	0.204	0.219	0.185	0.188	0.308
CII_REF_28	-0.032	0.004	-0.016	-0.075	-0.064	-0.057	-0.087	-0.124	-0.032	-0.050

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Table A.3 Length Variation ($\times 10^{-3}$) of the mixtures from 294 to 400 days.

Mixtures	Time (days)			
	322	350	378	400
CI_REF_7	-0.061	-0.043	-0.026	-0.049
CI_REF_28	-0.062	-0.084	-0.107	-0.101
CI_AF060_5%_7	1.670	1.872	1.977	2.081
CI_AF060_5%_28	0.390	0.398	0.405	0.507
CI_AF040_5%_28	0.515	0.574	0.633	0.730
CI_AR130_3%_7	2.475	2.954	3.136	3.317
CI_AR130_3%_28	0.985	1.752	2.519	2.674
CI_AR080_3%_28	-	-	-	-
CII_AR080_3%_7	-	-	-	-
CII_AR080_3%_28	-	-	-	-
CII_REF_7	0.385	0.385	0.421	0.387
CII_REF_28	-0.048	-0.051	-0.054	0.171

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