

# The effect of external sulfate attack on concrete, mortar and cement paste

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**Abstract.** The present work reports the results of an experimental campaign started two years ago and still ongoing, aimed to assess the behavior of different cementitious materials subject to external sulfate attack. To this purpose prismatic specimens of cement paste and specimens of mortar and concrete produced with the same Portland cement, were immersed in demineralized water and in different solutions containing 5% and 10% sodium sulfates. The expansion was monitored in time by direct length measurements and the degradation of the stiffness was indirectly obtained through non-destructive ultrasound wave propagation tests. XRD tests and SEM observations evidenced the presence of secondary gypsum in the outer part of the specimens were sulfates penetrated. An increase of the material porosity was also measured in this region.

## Introduction

Concrete durability depends not only on the material composition and on the resulting porosity, but also on the environmental conditions. In particular, when a concrete structure is in contact with sulfate-rich waters or soils, a series of complex chemical reactions can occur between the sulfates diffusing within the material and the aluminates of the cement paste, leading to leaching, secondary gypsum and ettringite formation, overall expansion and degradation of concrete. These phenomena are gathered within the general term of sulfate attack [1], [2]. Many works are devoted to the description of sulfate attack both from the experimental [3-6] and from the modeling [7-10] points of view. Several experimental campaigns on cement paste [3], mortar [4] and concrete specimens [5], [6], are reported in the literature, however the results are strongly dependent on the specific test conditions and the results on these three materials are therefore difficult to compare.

In the present work, we report the experimental results obtained on prismatic specimens partially immersed and fully immersed in sodium sulfate solutions and we introduce initial results on a more recent campaign, still ongoing, on cement paste specimens and mortar specimens prepared with the same cement and the same aggregates, with smaller maximum aggregate size. The final aim of this experimental program still in progress is to highlight the role of the aggregate size on the phenomenon.

The tests on concrete prisms, partially immersed in a 10% sodium sulfates solution, were numerically simulated, using the multi-phase damage model proposed in [9-10]. A good agreement is found both in terms of the overall expansion and of the degradation pattern.

## Experimental program

The experimental campaign, started 20 months ago, is conducted on prismatic concrete specimens of dimensions 8x8x16 cm. More recently also prismatic mortar and cement paste specimens of dimensions 4x4x16 cm were included in the experimental program. For all specimens a Portland

cement type CEM I 52.5R and siliceous aggregates are used, with maximum size of 16 mm for concrete and 4 mm for mortar. The chemical composition of the cement is given in Table 1.

Table 1 – Chemical composition of cement

Cement	$C_3A$	$C_4AF$	$SO_3$
CEM I 52.5R	4.22%	5.16%	3.61%

Studs for subsequent length measurements were directly inserted during casting in the smaller specimens (see Fig. 1a) while they were glued on the two bases and on the lateral faces of the larger specimens (see Fig. 1b).

The specimens were cured for 28 days in a climatic chamber at temperature  $T=20^{\circ}C$  and relative humidity  $RH=90\%$ . After curing, the samples have been stored in different conditions: concrete specimens have been fully immersed or partially immersed in pure water or in a solution with 10%  $Na_2SO_4$  concentration; mortar and cement paste specimens have been fully immersed in pure water and 5% and 10% sodium sulfate solutions.

The specimens are periodically extracted from the solutions, to measure the weight and length variations. The elastic modulus is also evaluated through non-destructive ultrasonic tests.

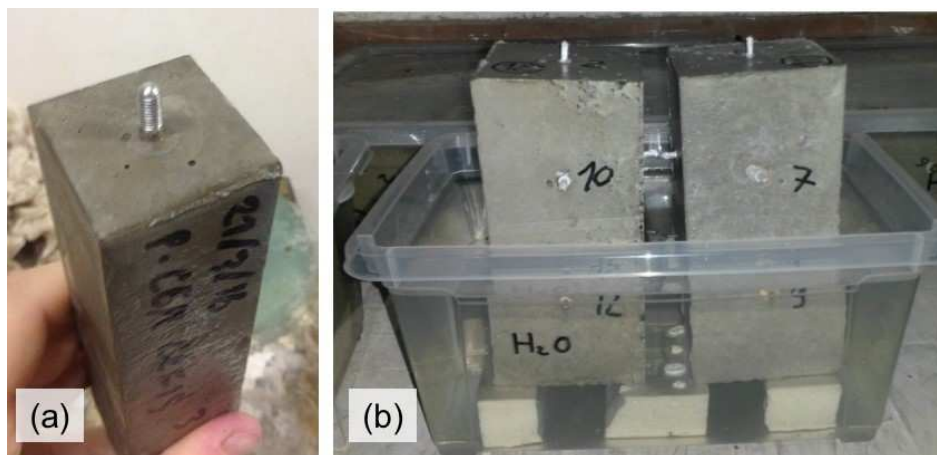


Figure 1- (a) Mortar sample with the stud, (b) concrete samples partially immersed.

## Experimental results

**Expansion and stiffness of concrete prisms.** Figure 2 shows the mean time evolutions of the longitudinal strains for the concrete specimens stored in different conditions. Initially all specimens expand due to water imbibition: the expansion is higher for the specimens fully immersed (lines yellow and light blue in Fig. 2) and is independent from the presence of  $Na_2SO_4$ . After about three months of exposure, the expansion of the specimens in water, both in fully and partially immersed conditions, stabilizes, while the specimens in sodium sulfate solutions continue to expand due to the chemical reactions (yellow and red curves in Fig. 2).

The longitudinal elastic modulus was indirectly measured by ultrasonic wave propagation tests at regular intervals between 400 and 600 days of immersion for concrete prisms stored in water and in sodium sulfate solution. The mean value of the dynamic elastic modulus is computed from the measured wave velocity by assuming a fixed value of the Poisson's coefficient, then the empirical reduction of 17% is applied to compute the static value.

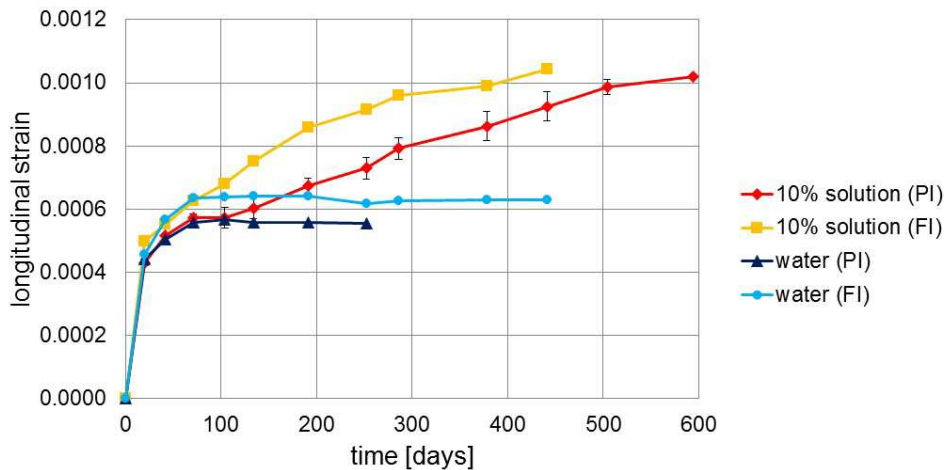


Figure 2 – Evolution in time of the longitudinal strain of concrete specimens in different storing conditions: fully immersed (FI) and partially immersed (PI) in water and in 10% sodium sulfate solution.

The results are shown in Fig 3, were also the values obtained for a specimen in air are plotted for reference. The presence of water causes an increase in the wave speed and therefore an increase of the apparent stiffness of the specimen in water with respect to the one in air. The sulfate attack damages the specimen stored the sulfate solution which exhibits a decrease of stiffness in the considered period.

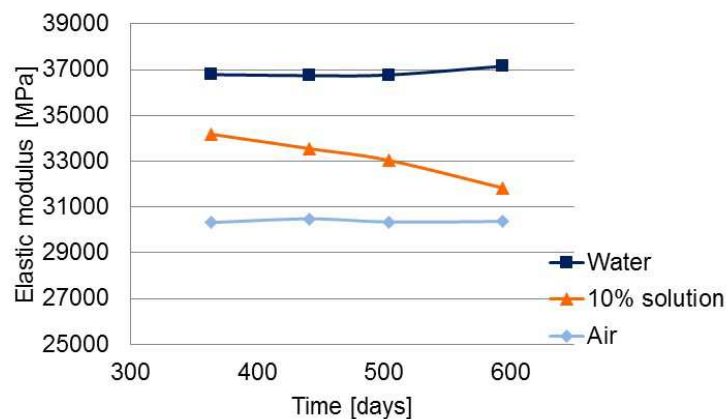


Figure 3 – Evolution in time of the longitudinal elastic modulus of concrete specimens in different storing conditions: in air, in water and in 10% sodium sulfate solution.

**Visual, porosimetry, SEM and XRD analyses of concrete after 400 days of immersion.** The concrete specimens after 400 days of immersion in the sulfate solution are significantly degraded. Macro-cracks are clearly visible on the external part of the prisms, see e.g. Fig. 4.

In order to characterize the effect of the sulfate attack, porosimetry measurements, XRD analyses and SEM observations were performed. To this purpose, a specimen stored in water and one stored in sodium sulfate solution were cut and different mortar samples were extracted. Samples A and B were taken respectively from the surface and from the internal part of the prism stored in water, samples C and D were taken respectively from the surface and from the internal part of the prism stored in the sulfate solution.

The porosity of the samples was obtained through a Micromeritics AutoPore IV 9500 series mercury intrusion porosimeter (MIP). A measuring pressure from 1.5 to 33000 psia was applied to the mortar samples, of dimensions 15mmx15mmx20mm. Figure 5 shows the values of the porosity and of the mass density of the samples A, B, C, D. Due to the sulfate attack occurred in the external

part of the specimen stored in sodium sulfate solution, the porosity of sample C is higher than in the other samples and the mass density is lower.



Figure 4 – Cracks pattern on a concrete specimen after 400 days of immersion in a 10% Na<sub>2</sub>SO<sub>4</sub> solution

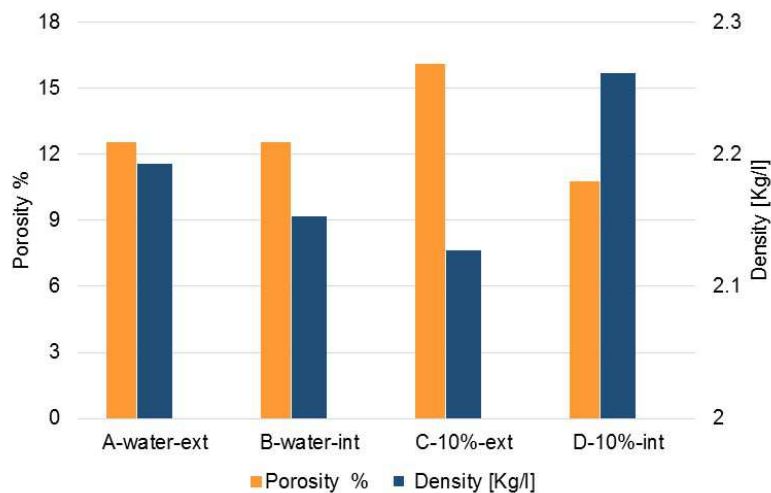


Figure 5 - Porosity (left axis) and mass density (right axis) of mortar samples taken from concrete prisms immersed in water and in sulfate solution for 400 days.

Figure 6 compares the pore size distribution of sample D, taken from the intact core of the specimen, blue curve, with that of sample C affected by the reaction, orange curve. It appears that the increase in total porosity of sample C is due to the formation of additional cracks and pores of a size above 10 micron, bigger than that typical of this material.

The cumulative pore radius distribution of the four samples is displayed in Fig. 7. While the two samples from the specimen stored in water have the same distribution, there is a significant difference between the pore distribution in the core and at the surface of the specimen stored in the aggressive solution. As already observed the difference is mainly due to the presence of pores of large size.

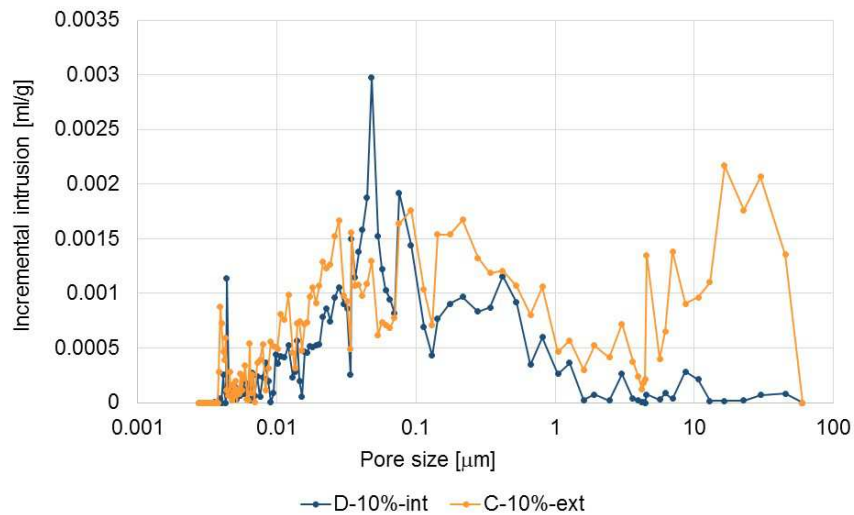


Figure 6 - Incremental pore radius distribution in mortar samples taken from the core (D) and the external part (C) of a concrete prism immersed in sulfate solution.

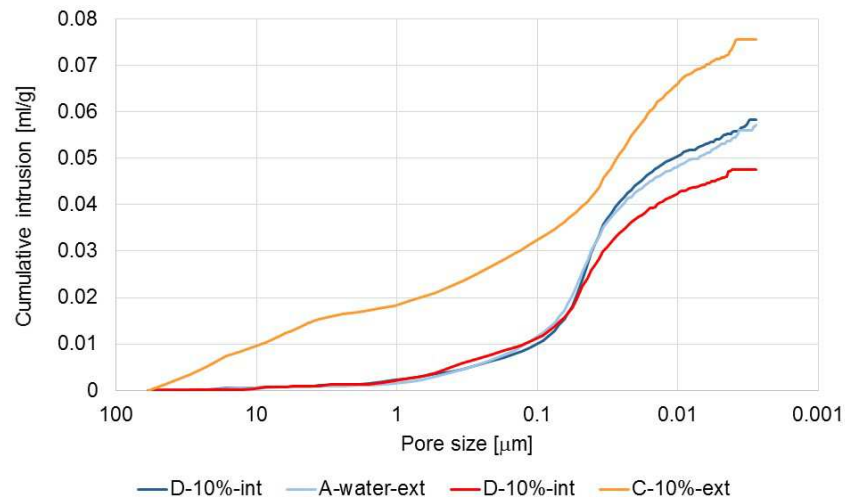


Figure 7 – Cumulative pore radius distribution in mortar samples taken from concrete prisms immersed in water (blue and light blue lines) and in sulfate solution (orange and red lines).

SEM observations and EDS spectra on samples taken from the outer part of the specimen stored in the sulfate solution (sample C) showed the formation of big crystals of gypsum, see Fig. 8. This result is in agreement with that reported in [11]: the formation of gypsum predominates at high concentration of sodium sulfate, as the one used in this work, while secondary ettringite formation is predominant at low concentration of sodium sulfate.

The presence of secondary gypsum in the outer part of the specimen affected by sulfate attack is confirmed by X-Ray diffraction measurements. Figure 9 shows the results on this sample (sample C), while Fig. 10 reports the result of XRD on a sample taken from the central part of the specimen (sample D). In the first sample besides the mineral of the aggregates (quartz, calcite, kyanite) also gypsum is present and it is reported in the table of constituents. The sample of the internal part of the specimen is not affected by the sulfate attack and no significant quantities of gypsum are found (see Fig. 10).

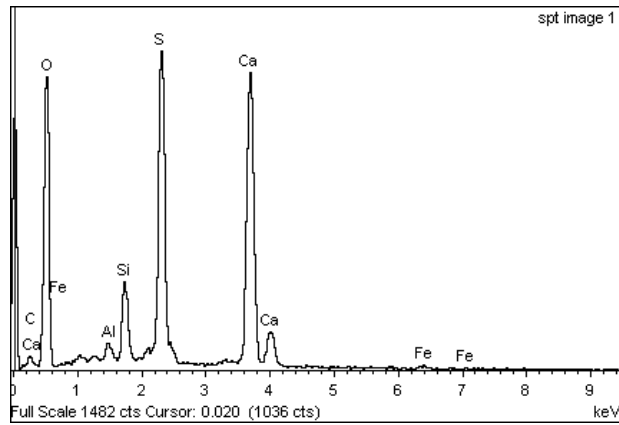
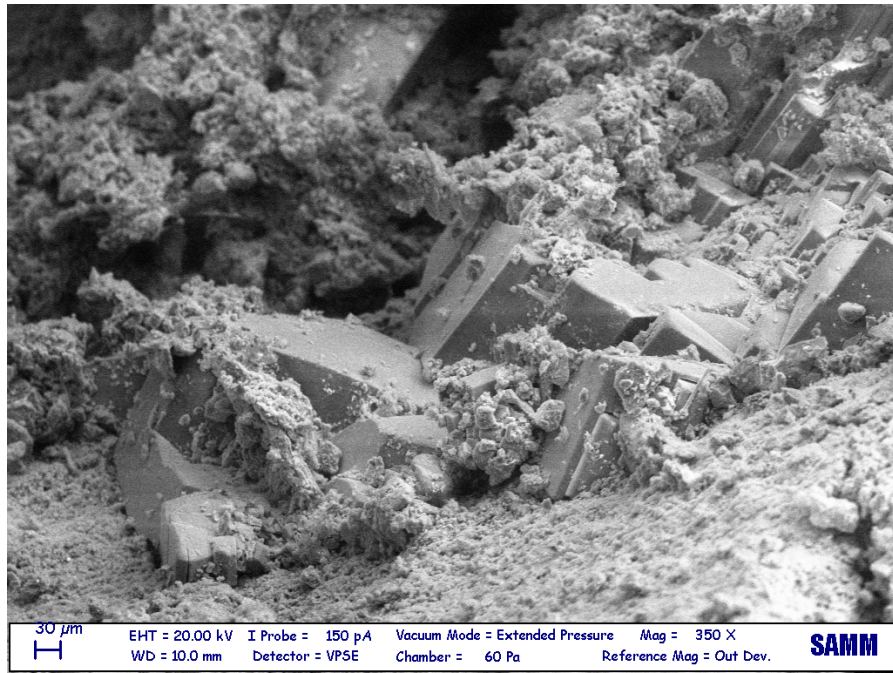


Figure 8 – SEM image of sample C with crystals of gypsum formed due to sulfate attack and corresponding EDS.

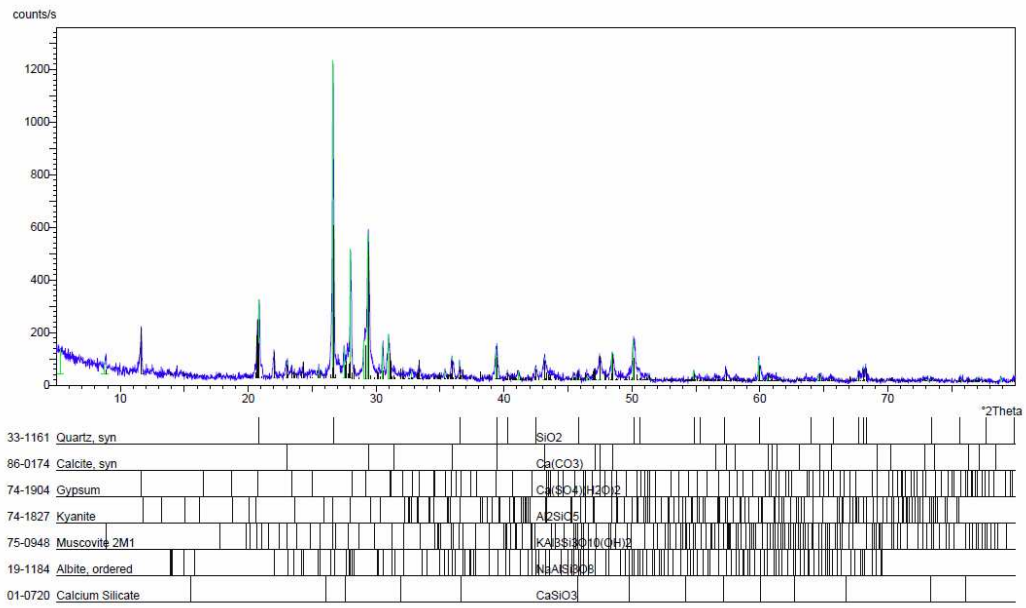


Figure 9 – XRD of mortar powder of the external part of the specimen after 400 days of immersion in 10% sodium sulfate solution.

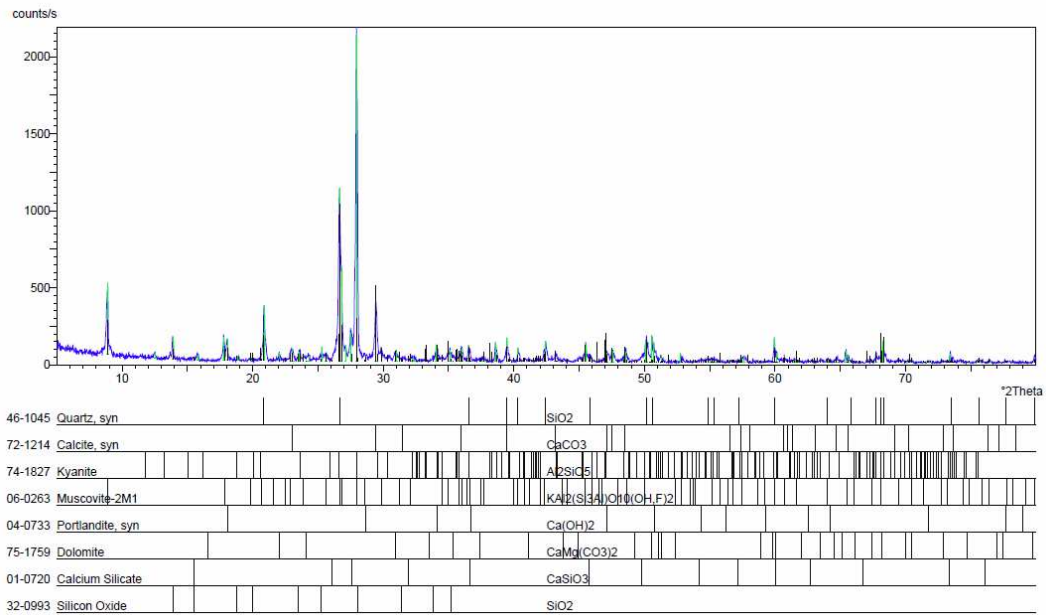


Figure 10 – XRD of mortar powder of the internal part of the specimen after 400 days of immersion in 10% sodium sulfate solution.

**Expansion of mortar and cement prisms.** The prisms of mortar and cement paste were produced more recently and they have been immersed in water, 5% and 10% sodium sulfate solutions about three months ago, therefore the expansions, even in water, are not stabilized yet. Figure 11 shows the mean expansions curves together with the standard deviation of mortar specimens in different solutions: a similar evolution is observed up to now since the reaction probably is not yet occurred.

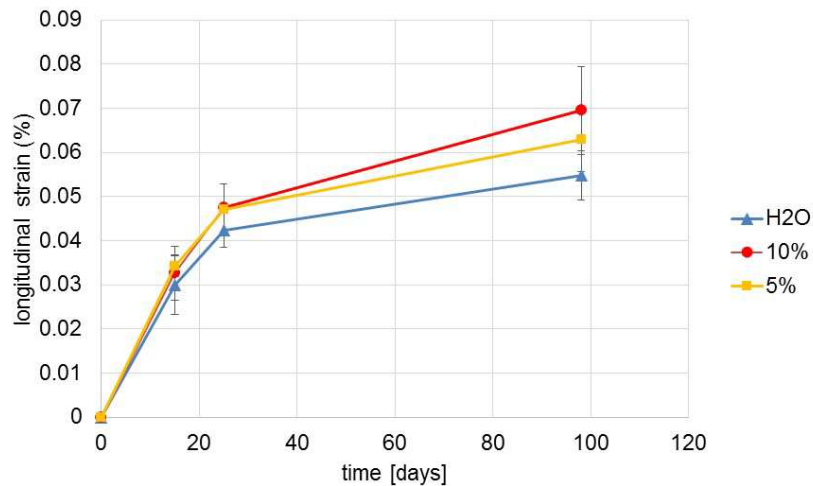


Figure 11 – Evolution in time of the longitudinal strain of mortar specimens in different storing conditions: water, 5% and 10% sodium sulfate solutions.

Figure 12 shows a preliminary comparison of the expansion in the three different materials, but the campaign should be pursued to draw any conclusion.

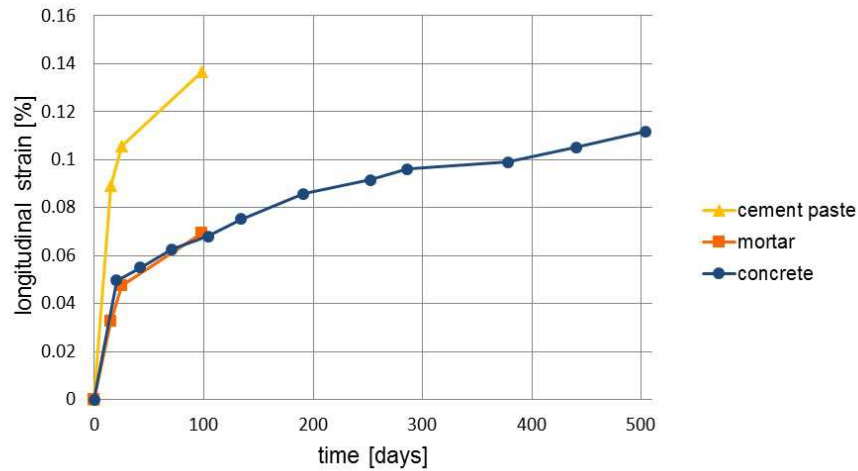


Figure 12 - Longitudinal strain of prisms of concrete, mortar and cement paste immersed in 10%  $\text{Na}_2\text{SO}_4$  solution

### Numerical simulations

The sulfate attack on the concrete specimens has been simulated using the multi-phase damage model proposed in [9] and further developed in [10]. In this model, concrete is described as a multiphase material made of a solid skeleton, a fluid phase including water and air and an expanding phase, which exerts a pressure on the solid skeleton. The degree of saturation is computed through a simplified diffusion model and then a reactive-diffusion model allows for the computation of the expansive products of the reaction occurring between the aluminates of the cement paste and the incoming sulfate ions. Finally a mechanical analysis allows to compute the expansion and the degradation of the specimens. Two damage variable are introduced accounting for both chemical and mechanical damage. It should be remarked that, even though in [9-10] the expansive product considered is secondary ettringite, the model is here tuned and employed as a first approximation, to simulate the mechanical effect of the sulfate attack also in the presence predominant gypsum formation.

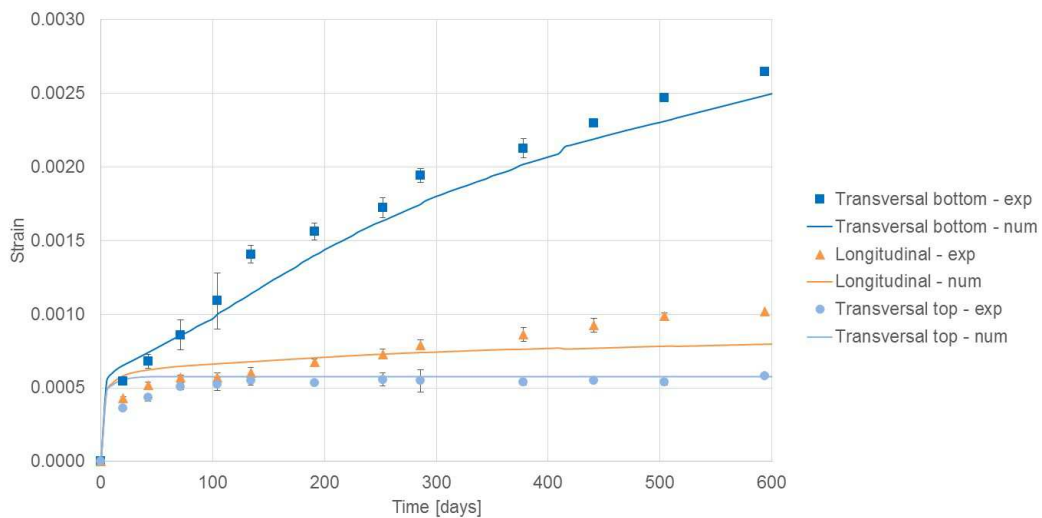


Figure 13 - Longitudinal and transversal strain of prisms of concrete, partially immersed in 10%  $\text{Na}_2\text{SO}_4$  solution: experimental points and numerical prediction

Figure 13 displays the comparison between the numerical predictions and the experimental data of strain evolution in partially immersed concrete prisms; the transversal strain in the immersed portion of the specimens continuously grows in time due to the reaction development, while the



transversal strain of the portion in air initially grows due to the capillary rise of water and then stabilizes, the longitudinal strain has an intermediate growth. The numerical prediction is in good agreement with the real expansion.

The numerical analyses predict the development of both chemical damage, which starts from the outer skin of lower half of the specimen, and mechanical damage which localizes inside the specimen near the corner, see Fig 14. The highly damage zone corresponds qualitatively to the zone of crack formation experimentally observed, as shown by the picture on the same figure.

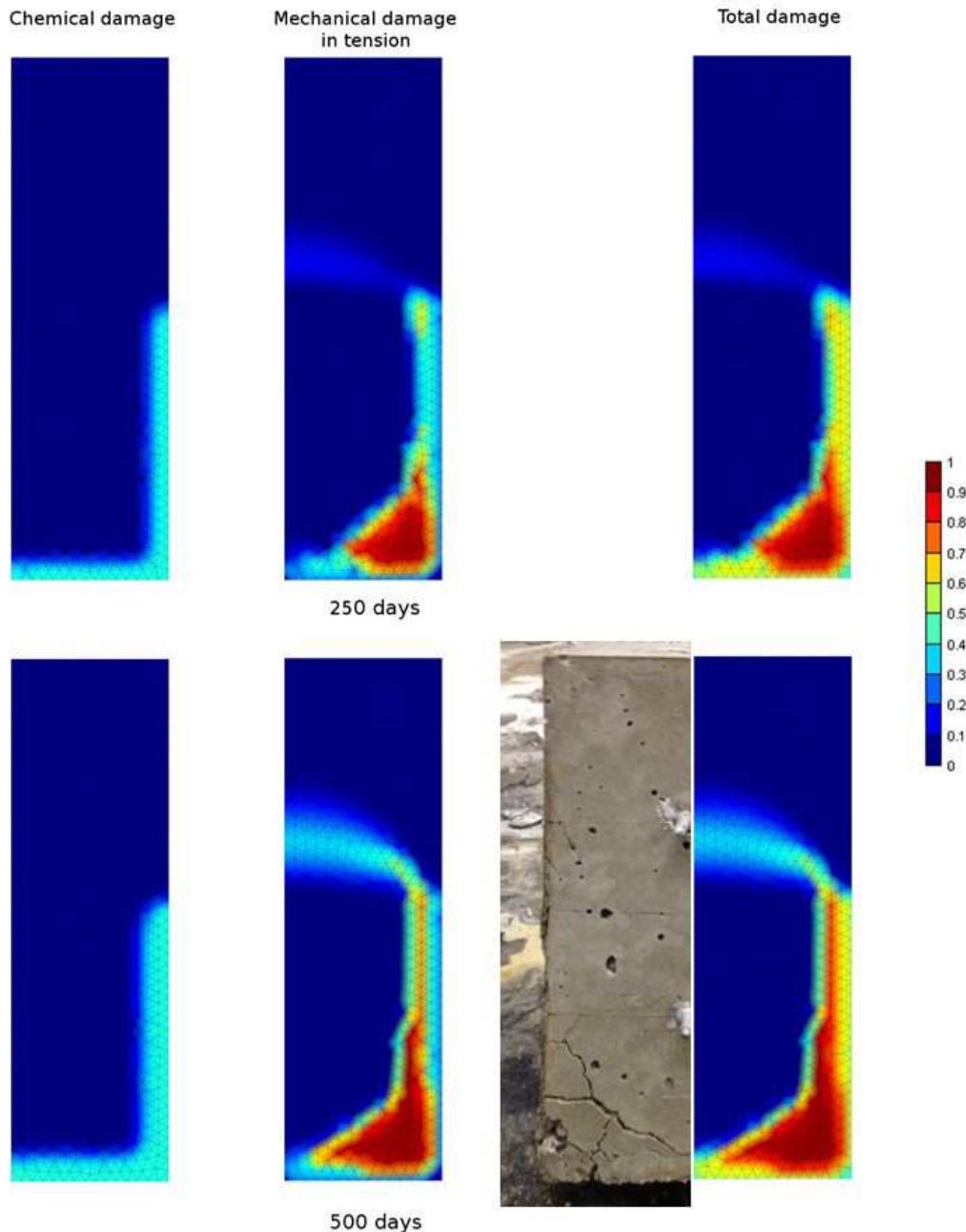


Figure 14 – Chemical, mechanical and total damage patterns after 250 and 500 days of partial immersion in in 10% Na<sub>2</sub>SO<sub>4</sub> solution (only half specimen is displayed).

### Conclusions

The experimental results obtained in this work on concrete specimens showed that the sulfate attack after 15 months of immersion produced: *i*) an increase in porosity, in particular and increase of pore of large size, *ii*) a significant crack formation mainly in the circumferential direction, *iii*) an overall

expansion. XRD and SEM observations have shown that the predominant expansive product is secondary gypsum. The mortar samples seem to exhibit a behavior similar to concrete while the cement paste showed a higher strain, but the campaign should be pursued to have a clear view on this point.

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