Influence of the microstructure properties on the degradation of concrete submitted to external sulphate attacks

Emmanuel Rozière, Frederic Grondin, Ahmed Loukili

Influence of the microstructure properties on the degradation of concrete submitted to external sulphate attacks

Emmanuel Rozière, Frédéric Grondin, Ahmed Loukili

Institut de Recherche en Génie Civil et Mécanique (GeM) – UMR CNRS 6183, Centrale Nantes, Nantes Altlantique Universités, France.
frederic.grondin@ec-nantes.fr

Abstract. The study presented in this paper is aimed at developing experimental and numerical tools to assess performances of concrete exposed to sulphate attacks. The experimental test is applied to mortars in order to compare different binders. It consists in immersing mortar specimens in sodium sulphate solution and monitoring mass, expansion and elastic modulus. It showed significant differences between low and high C_3A cements and between Portland and blended cements. On the other hand, simulations based on a finite difference model and homogenization methods have been performed and compared to experiments. Results are sensitive to the degree of hydration of cement phases and microstructure properties. It showed that this approach is able to take into account changes in chemical composition of the binder and of the mortar mixtures.

Keywords: mortar, sulphate attacks, modelling, multiscale, settlement.

1 Introduction

Concrete structures are exposed to sulphate ions in sea water and ground water. The kinetics and the mechanisms of degradation depend on the conditions of the exposure of concrete to a sulphate solution, namely: the associated cation (sodium, calcium, or magnesium), the sulphate concentration and the pH of the solution, as shown by Neville (2004) and Dehwah (2007). The mechanism of degradation in sodium sulphate solution has been described by Duval and Hornain (1992), Irassar et al. (2003), Planel et al. (2006). Sulphate ions diffuse in the porosity of concrete and react with some hydration products. Generally, the macroscopic degradation is observed after a swelling phenomenon of the specimen. The swelling is due to the expansive secondary ettringite formation in pores. When the limit expansion of the pore is reached, microcracks nucleate in the cement paste surrounding the pore. This finally causes a decrease of the stiffness of concrete. Even for high sulphate concentrations, the propagation of the sulphate attack into concrete takes several months or years. So accelerated tests and predictive models have to be developed to assess performances of concrete under these severe conditions. Macroscopic models have been developed in the objective to compute the strain expansion and the damage of

concrete submitted to sulphate attacks (Snyder et al., 1995, Tixier and Mobasher, 2003). These models are used to compute the ettringite formation according to the diffusion of sulphate ions and the degradation of concrete. Moreover, micromechanical models have been suggested based on diffusion-reaction equations (Boehm and Rosen, 1997, Krajcinovic et al., 1992). But no models take into account the hydration of the residual cement clinkers which can occur during the degradation by the water filtration in cracks.
In this study a performance test has been developed from standards NF P 18-837 (1993) and ASTM C 1012 (2000) to qualify the choice of the binder on mortars submitted to sulphate attacks. In the objective to study the influence of the microstructure properties on the durability of concrete under these conditions, multiscale approaches are used to determine the macroscopic elastic properties of the material from its local behaviour. Simulations have been compared to test results on twelve different mortar mixtures.

2 Experimental program

2.1 Cementitious materials

The test was designed to assess chemical resistance of cements or binders of concrete exposed to sodium sulphate attacks. Three reference cements were used, namely:

1. Portland cement CEM I 52.5 R (high C_3A content: 10.6%)
2. Sulphate resisting Portland cement CEM I 52.5 N PM ES (low C_3A content: 2%)
3. Sulphate resisting blended cement CEM III I 42.5 PM ES made of 62% ground granulated blast-furnace slag (GGBS)

Their compositions are significantly different, so they may be used as reference binders to study the sensitivity of the test. Three other binders were designed to investigate the effect of the chemical composition of binders on sulphate resistance of concrete:

4. Portland cement CEM I 52.5 R (high C_3A content: 7.5%)
5. Portland cement CEM I 52.5 R (4) + 62% GGBS
6. Sulphate resisting Portland cement CEM I 52.5 N PM ES (2)+ 30% Fly Ash

2.2 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
Cement1	495						419			591		
Cement2		498				368		420			597	
Cement3			497						420			593
Cement4				497	190							
GGBS					316							
Fly ash						158						
WRA					4.4							
Water	247	249	248	248	237	231	272	273	273	207	209	208
w/b	0.50						0.65			0.35		

Table 1. Mortar mixtures.

The twelve mortars mixtures given in Table 1 were designed keeping the paste volume (water + binder volumes) constant. The six previously described binders were respectively used in M1-M6 mortars mixtures, keeping water/binder (w/b) ratio constant.

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.

2.3 Test procedures

For each mortar mixture, six 4x4x16 cm^3 prismatic specimens and six 2x2x16 cm^3 specimens were cast and sealed cured for 24 hours. 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 specimens were saturated with sodium sulphate solution and immersed in the solution. The sulphate concentration is 30 g/L. The solution is prepared with demineralised water and changed once a month. 2x2x16 cm^3 specimens have gage studs to measure expansion with length comparators. The elastic modulus was determined on 4x4x16 cm^3 prisms with a *Grindosonic* apparatus. This device gives the frequency of a vibration created by a slight shock on the sample and the elastic modulus is calculated from this frequency with the Spinner and Teft model. All tests are carried out on three samples and the given results are average values.

3 Description of the numerical model

The model Sulfate2 developed by Tixier and Mobasher (Tixier and Mobasher, 2003) has been retained to model the strain evolution and the damage of concrete submitted to sulphate attacks. This model is based on the diffusion of the sulphate solution – calculated by a finite difference method – and the ettringite formation occurring in concrete. The diffusion of sulphate ions is calculated according to the Fick's law:

$$\frac{\partial U}{\partial T} = D(w)\frac{\partial^2 U}{\partial X^2} - kU \qquad (1)$$

With U is the sulphate concentration, k the solubility speed of sulphate and $D(w)$ the diffusion coefficient depending on the damage variable w. When the swelling ettringite fills a pore, a deformation ε_v^t is generated in the pore wall as follow:

$$\varepsilon_V^t = \varepsilon_V^0 - f\phi = C_{ar}\sum_P\left(\frac{\Delta V}{V}\right)_P - f\phi \qquad (3)$$

Where C_{ar} is the reacted aluminate concentration and P the product phase. F is a constant parameter dependent to the material tested. It has to be determined numerically in order to define the capillary porosity which can be filled by ettringite. The volume of C_3A is calculated by solving the stochiometric equations of the hydration of cement (Bernard et al., 2003). A multiscale approach, based on the self-consistent method, has been retained to calculate the Young modulus of the undamaged concrete. But this model is limited by the difficulty to take into account the new hydration of the residual clinkers occurring by the water filtration in cracks during the test.

4 Test results

Expansion, mass and elastic modulus have been monitored for one year and results are given on figures 1 to 3 for mortar mixture M4. This mortar mixture is made of cement 4, which has high C_3A content. Typical swelling due to sulphate attack is observed and significant expansion has been measured after 60 days of immersion (Figure 1). Elastic modulus (Figure 2) does not appear as a sensitive indicator of damage, as the modulus of attacked specimens remains equal or higher than modulus of sound specimens even if significant expansion and damage can be observed. Lee et al. (2005) and Sahmaran at al. (2007) have also shown the positive effect of sulphate attack on mechanical properties, before they finally decrease. As absorption of water and hydration are likely to occur after immersion, differences between measures on control specimens and attacked specimens were calculated to focus on the effects of sulphate ions. They are plotted on Figure 3. Relative mass decrease occurs during the period of latency, when no significant expansion is measured. It is mainly due to leaching and diffusion-reaction processes between sulphate solution and hydration products in cement matrix, as shown by Planel (2006). Mass increase is due to swelling of damaged mortar specimens. As the sulphate attack is external, the effect of the Exposed surface/Specimen volume ratio can be observed (Figure 3). Even mortars including sulphate resisting cement show significant expansion (Table 2). Analysis of microstructure would be necessary to know whether expansion is actually due to ettringite. Tian and Cohen (2000) have shown that gypsum could also cause expansion in sulphate environments.

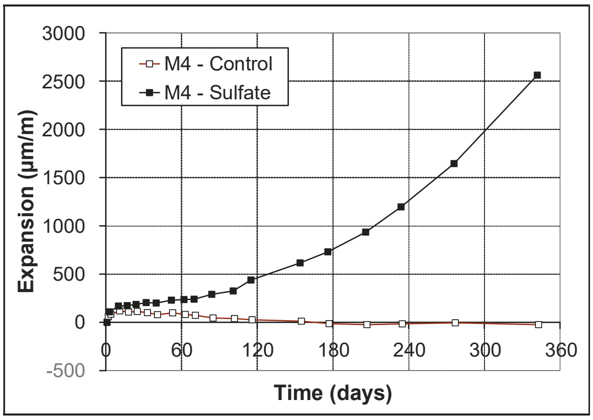

Figure 1. Expansion of 2x2x16 cm^3 specimens.

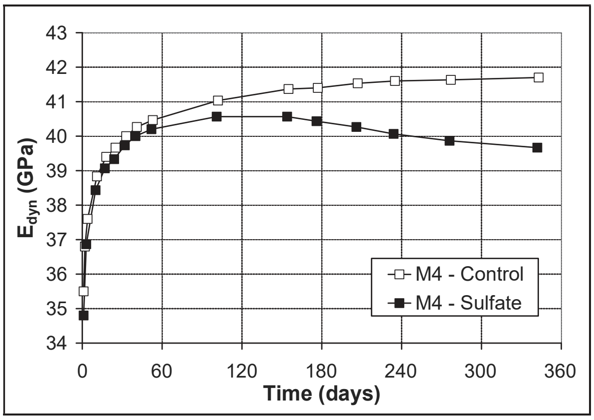

Figure 2. Elastic modulus of 4x4x16 cm^3 specimens.

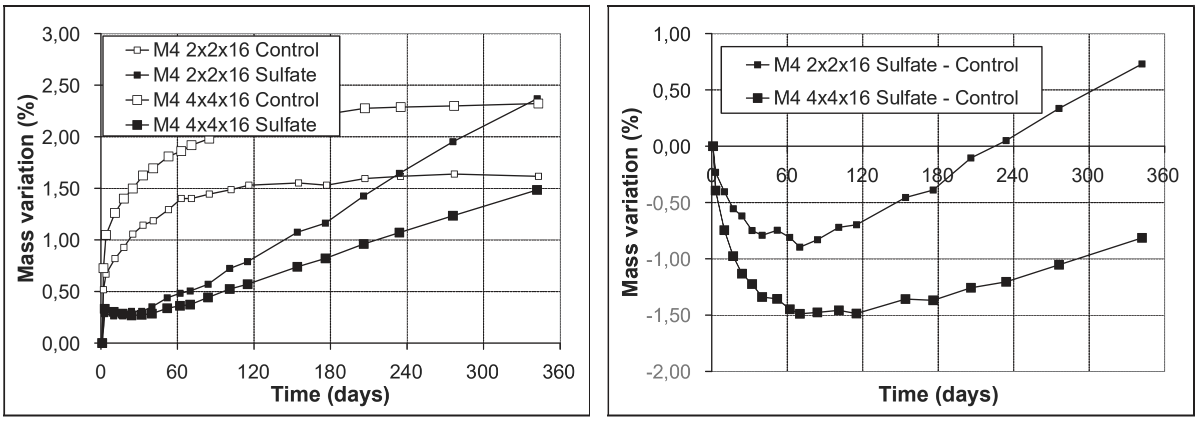

Figure 3. Mass variations of specimens.

Expansion (µm/m)	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
After 180 d. (µm/m)	285	1247	1576	752	224	206	310	1415	*	308	292	247
After 360 d. (µm/m)	319	3054	*	2811	301	489	168	3075	*	362	347	321

* Broken specimens

Table 2. Expansion of 2x2x16 cm^3 specimens.

5 Results of the numerical simulations and discussion

The model results are compared in a good agreement to experimental measurements (Figure 4). Diffusion coefficient of mortar, fraction of capillary porosity that can be filled, degree of reaction of cement and degree of reaction of C_3A were first varied in order to reproduce evolution from experiments. Such parameters are not easily available from tests. Moreover the response of the model is very sensitive to these parameters: example is given for M3 mortar mixture in Figure 4. So they must be assessed accurately through other methods.

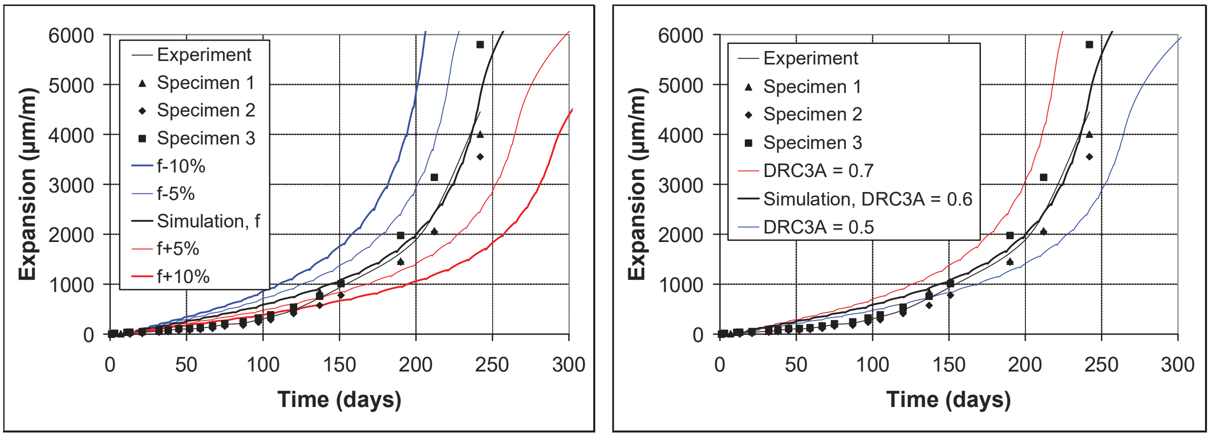

Figure 4. Sensitivity of simulated expansion to Fraction of capillary porosity that can be filled by expansive products *f* (left) and Degree of reaction of C_3A *DRC3A* (right).

6 Conclusions and perspectives

The experimental and the experimental tools have been applied to twelve different mortars mixtures exposed to sulphate attack for one year to investigate their ability to assess performances of concrete exposed to external sulphate attacks. The accelerated test is sensitive enough to show significant differences taking into account scatter of results. The mortars made of the three reference cements (Portland cements CEM I and CEM I PM ES, blended cement CEM III PM ES) actually showed different behaviours. High substitutions rates of cement by fly ash and slag resulted in enhanced performances of mortar. The most sensitive test indicator is expansion or mass variation due to swelling. Global elastic modulus is not affected during the first stage of attack. The test can be accelerated by increasing the water/binder ratio, but as a consequence it is not able to take into account compensating effects of chemical reactivity of binder and compactness of concrete. In the objective to have a model which no depends on the calibration of parameters, a model based on the multiscale approaches is under development which is based on the microstructure properties and on intrinsic parameters.

References

Neville A. (2004) The confused world of sulphate attack on concrete, Review, *Cement and Concree Research* 34, pp. 1275-1296.

Dehwah H.A.F. (2007) Effect of sulphate concentration and associated cation type on concrete deterioration and morphological changes in cement hydrates, *Construction and Building Materials* 21, pp 29-39.

Duval R., Hornain H. (1992) Chapitre 9 : La durabilité du béton vis-à-vis des eaux agressives, *In La durabilité des bétons*, Pressses de l'ENPC, France, 1992.

Irassar E.F., Bonavetti V.L., Gonzalez M. (2003) Microstructural study of sulphate attack on ordinary and limestone Portland cements at ambient temperature, *Cement and Concrete Research* 33, pp. 31-41.

Planel D., Sercombe J., Le Bescop P., Adenot F., Torrenti J.-M. (2006) Long-term performance of cement paste during combined calcium leaching-sulphate attack : kinetics and size effect, *Cement and Concrete Research* 36, pp. 137-143.

ASTM C 1012-95a (2000) Standard test method for length change of hydraulic-cement mortars exposed to a sulphate solution, *In: Annual Book of ASTM Standards, volume 04.01 cement; lime; gypsum*.

NF P 18-837 (1993) Produits de calage et/ou scellement à base de liants hydrauliques, Essai de tenue à l'eau de mer et/ou à l'eau à haute teneur en sulphates, AFNOR (French Standard).

Snyder, K.A., Clifton J.R., Pommersheim J. (1995) Computer program to facilitate performance assessment of underground low level waste concrete vaults, *In: Scientific Basis for Nuclear Waste Management XIX*, W.A. Murphy and D.A. Knecht, Eds., Materials Research Society, Pittsburgh, pp. 494-498.

Tixier R., Mobasher B. (2003) Modeling of damage in cement-based materials subjected to external sulphate attack. I:Formulation, *Journal of Materials in Civil Engineering*, 15 (4), pp. 305-313.

Tixier R., Mobasher B. (2003) Modeling of damage in cement-based materials subjected to external sulphate attack. II: Comparison with experiments, *Journal of Materials in Civil Engineering*, 15 (4), pp. 314-322.

Boehm M. and Rosen ..G. (1997) Global weak solutions and uniqueness for a moving boundary problem for a coupled system of quasilinear diffusion-reaction equations arising as a model of chemical corrosion of concrete surfaces, Preprint series: Institut für Mathematik, Humboldt-Universität, Berlin, 1997.

Grondin F., Dumontet H., Ben Hamida A., G., Boussa H. (2007) Multi-scales modelling for the behaviour of damaged concrete, *Cement and Concrete Research* 37, pp. 1453-1462.

Krajcinovic D., BasistaM., Mallick K., and Sumarac D. (1992) Chemo-micromechanics of brittle solids, J. Mech. Phys. Solids, 40, 5, pp. 965-990.

Spinner E. and Teft W.E., A method for determining mechanical resonance frequencies and for calculating elastic modulus from these frequencies, *In Proceedings ASTM*, ASTM.

Lee S.T., Moon H.Y., Swamy R.N. (2005) Sulphate attack and role of silica fume in resisting strength loss, *Cement and Concrete Composites* 27, pp. 65-76.

Sahmaran M., Kasap O., Duru K., Yaman I.O. (2007) Effects of mix composition and water-cement ratio on the sulphate resistance of blended cements, *Cement and Concrete Composites* 29, pp. 159-167.

Tian B., Cohen M.D. (2000) Does gypsum formation during sulphate attack on concrete lead to expansion?, *Cement and Concrete Research* 30, pp. 117-123.