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Parametrical study of the cementitious materials degradation under external sulfate attack through numerical modeling

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HIGHLIGHTS

- Numerical simulations were used to improve the design of sulfate attack testing.
- Aluminate and sulfate are considered in order to understand the cracks mechanism.
- Great influence of boundary conditions on degradation rate and the formed products.

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ABSTRACT

Underground concrete structures may be subjected to external sulfate attack and their long-term performance is of concern. A coupled transport/chemical numerical model has been compared to experimental data obtained on a cement paste exposed to external sulfate attack thanks to recent developments in experimental analysis such as scanning electron microscopy and image analysis that provided total ion concentration profiles for a given species in cement paste specimens. As other studies the model succeeded in calculating the position of the ettringite precipitation front and the position of the first decrease due to the portlandite dissolution whereas the leaching of portlandite and ettringite was not accurately assessed in the first millimeters because of the necessity to take into account change of the transport properties in the degraded zone. Then a numerical parametric study was carried on. The influence of permanent solution renewal, pH control, and dissolved CO_2 concentration were analyzed. The accelerating effect of permanently renewing the solution was confirmed. The influence of the pH control was found dependent of the renewing of solution. The presence of CO_2 did not play a significant role.

1. Introduction

The presence of sulfate in groundwater affects the durability of cement-based materials. Sulfate propagates into the material and modifies transport and mechanical properties, which is called External Sulfate Attacks (ESA). Even after the complete hydration of cement paste the interstitial solution of mortar or concrete is actually in a metastable thermodynamic equilibrium with the various solid phases. The ingress of external sulfate changes the chemical composition of the interstitial solution and disturbs the local thermodynamic equilibrium. Then dissolution and precipitation reactions might occur. Dissolution of hydration products mainly affects Portlandite $Ca(OH)_2$. The increase of sulfate concentration in interstitial solution results in the formation of ettringite ($C_3A{\cdot}3CaSO_4{\cdot}26H_2O$ – AFt). The leaching of portlandite and ettringite crystallization pressure cause an increase in porosity, expansion, cracking, and consequently a loss of mechanical properties and an increase in permeability. The usual way of preventing ESA is to reduce C_3A and C_3S contents. Mineral admixtures such as slag and fly ash are often used to improve the durability of cement-based materials exposed to sulfate attacks. The mineralogical composition of mineral admixtures is likely to vary, resulting in different levels of resistance to external sulfate attacks, but common mechanisms can be observed. Low-calcium fly ash and slag act at three different levels. As the Portland cement content is reduced, the C_3A content, and the initial $Ca(OH)_2$ content provided by the hydration of cement, are lower. The hydration of slag and the pozzolanic reaction consume $Ca(OH)_2$ in cementitious matrix. Such reactions produce denser hydration products, such as CSH, thus lower permeability. Our study mainly deals with Portland cement but other works explain how supplementary cementitious materials such as fly ash and slag influence the resistance of concrete to sulfate attack [1,2]. Other studies have shown that the

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influence of fly ash and slag on sulfate resistance depends on exposure conditions, for instance, the nature of the associated cation (e.g., Mg^{2+}, Ca^{2+}, Na^{+}) [3] and wetting and drying cycles [4]. As a consequence it is necessary to understand the influence of exposure conditions on chemical and physical phenomena involved in sulfate attacks to design reliable tests.

ESA have been studied for a long time. Laboratory testing procedures have been carried out to compare the resistance of cement-based materials to ESA. It is often assumed that performance and service life correlate with indicators deduced from short-term accelerated tests. Acceleration can result from increasing sulfate concentration, increasing temperature, decreasing pH [5] or applying an external electrical field [6]. Nevertheless, the representativity of these tests is still discussed [7]. One reason can be the large number of factors that can influence not only the degradation rate but also the mechanism of degradation. Another reason is that factors can depend on each other. Moreover the indicators deduced from sulfate attack testing mainly deal with mechanical and physical behavior, namely: expansion, strength, elastic modulus, and permeability. However the same physical degradation, for instance cracking or increase in permeability can be due to several mechanisms of degradation.

There are several number of studies dealing with thermodynamic modeling coupled with transport models for describing sulfate attack and its consequences in terms of precipitation/dissolution of mineral phases [8,9]. Marchand et al. described the theory of the coupling procedure [8]. Other studies focused on comparisons between numerical results and experimental data [10–12]. Some interested in the choice of the transport equations and concluded that a Nernst–Planck description for the transport of the species seems to be a good choice [10,13] or at least a multi-species fickian approach [10]. Today, it seems to be interesting to propose a parametrical study of such a coupled model in order to improve its behavior and to show the necessity or not to take into account several conditions (e.g. renewal of the aggressive solution, presence of dissolved CO_2 in the solution, control of the solution pH).

This study aims at contributing to understand the complex mechanisms that drive ESA during sulfate attack testing in controlled exposure conditions [14]. A chemical transport coupling numerical model has been used on simple procedure [15]. The model have been modified and intended for ESA problems in this work. Simulations might also have been performed by other coupling software as Hytec [16] or ToughReact [17]. Nevertheless, the softwares used in the present coupling procedure and in particular Comsol gives the possibility to include the material mechanical behavior for further studies.

Numerical results actually show changes in chemical species concentrations and dissolution/precipitation fronts inside the material that are difficult to assess experimentally. However recent developments in SEM-EDX technique and X-ray microtomography provide useful information dealing with chemical changes in cement paste. Moreover the sulfate attack testing presented in this study allows determining the amounts of calcium and sulfate ions that are leached or ingress in the cement paste specimens.

This paper first presents a comparison between total concentrations of calcium, aluminium and sulfur (Ca, Al and S) profiles deduced from SEM-EDX and simulated by the model. Then a numerical parametric study is proposed to quantify the different factors influencing sulfate ingress, precipitation of phases or dissolution rates. Three parameters have been studied. The first one is the effect of renewing the sulfate solution [9]. The experimental procedure actually ensures that the solution is renewed at regular intervals. The numerical model aims to quantify this effect. The second parameter is the pH, which can be controlled or not by adding nitric acid. This latter quantity is actually assumed to be directly related to the amount of calcium leached from the cement paste, as it is the case for calcium leaching in pure deionized water [18]. Previous study has underlined the importance of controlling the pH on the degradation rate [9,19]. The third one is the influence of dissolved CO_2 in samples immersing solution. The solution is generally in equilibrium with atmospheric pressure and air with CO_2.

The simulation is viewed here as another kind of experimental system and should be analyzed as such. That is to say that, the model is tested to define its reliability and, if successful, it is considered to provide understanding of the modeled phenomena. For this purpose, Section 2 describes the experimental procedure. In Section 3, the model and hypotheses are exposed, including the chosen cement paste hydration composition and adopted transport equations. Results are then compared to experimental data in Section 4. Finally, the numerical parametric study is presented.

2. Experimental procedure

2.1. Sulfate attack testing

The test was conducted on Portland cement paste with a water/cement ratio of 0.4. The chemical composition of cement is given in Table 1.

Two cement paste samples were immersed for at least 160 days in a Na_2SO_4 solution (3 g/L sulfate concentration), as shown in Fig. 1 [20]. The cylindrical specimens were 160 mm high and 20 mm in diameter. They were coated on their both ends with a water-proof vinylester resin, thus exposed to sulfate attack only on their circumferential surfaces. They were immersed in 1.7 L sodium sulfate solution tank after 28 days of water curing.

As pH tended to increase because of the dissolution of portlandite $Ca(OH)_2$, 0.5 mol/L nitric acid was added to control the pH of the sulfate solution at a constant value pH = 7.5. The solution was renewed every 15 mL of added nitric acid. Its calcium and sulfate concentrations were determined using ionic chromatography.

2.2. Microtomography

XRadia MicroXCT-400 system was used to observe samples after 160 days of sulfate attack. The energy used was 110 kVp X-rays. Successive rotations of the sample, 2000 projections, corresponding to 2000 angular positions ranging between 0 and 360, were acquired by a 4 megapixel (2048 × 2048) CCD-digital camera and an objective revolver, that can be used to choose the desired magnification. Filters were used to compensate for beam hardening. The pixel size was 28 μm and the exposure time was 4 s for each image. The data scanned with the Xradia device was reconstructed with Xradia's own software.

2.3. Scanning Electron Microscopy

SEM investigation was used to analyze the micro-structure of the sulfate attacked specimens. The Jeol JSM-6060 LA microscope was also equipped with an energy dispersed X-ray analysis and X-ray Mapping. The observations were performed by back-scattered electrons imaging. The pressure in the specimen chamber was 50 Pa and the accelerating voltage was 15 kV. The specimens used for SEM observations were 3 cm thick slices from the $2 \times 2 \times 16\ cm^3$ mortar prisms. They were dried for two days at 20 C, 50% H.R and then embedded in a low modulus epoxy resin. The specimens were then polished using progressively finer grids.

Table 1
Chemical composition of CEMI 52,5N CE CP2 NF cement.

Oxide	Quantity (wt.%)
SiO_2	20.6
Al_2O_3	5.3
Fe_2O_3	2.11
CaO	66.3
MgO	1.09
K_2O	0.28
Na_2O	0.18
SO_3	3.3
Other	0.84