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Local study of the corrosion kinetics of hardened Portland cement under acid attack



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ABSTRACT

Whereas the chemical reactions occurring during the acid corrosion of cementitious materials are now well known, their reaction rates have still not been measured. We propose here a methodology using digital holographic interferometry to access to these pure surface reaction rates. This method makes possible the differentiation between the dissolution and precipitation steps. We use it to measure the reaction rate constant of the dissolution of hardened Portland cement in aqueous solutions of nitric, sulfuric and hydrochloric acids at pH 2. This quantity is seen to be unexpectedly similar for the three acids, with a value of the order of $1 \text{ mg/m}^2/\text{s}$. We have measured the evolution of this reaction rate constant with the pH in nitric acid. We have also measured the real pH of the solution at the material surface, which is always alkaline ($\text{pH} > 11$), even for attacks by solution with pH as low as 1.

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1. Introduction

The extension of the durability of concrete buildings necessitates the understanding of its limiting factors, like creep, crack propagation by water freezing, degradation due to aggressive environments, etc. Among chemical attacks reducing the service life of construction materials, acid attack is particularly detrimental to materials as alkaline as cementitious materials. Indeed the hydration products of cement are neutralized by protons, inducing dissolution and precipitation of new salts, destroying the microstructure of this hydraulic binder. The mechanisms of action of acid reagents on concrete, mainly originating outdoor in air pollution (dry deposition) and acid rains (wet deposition), have been investigated for a few decades, and the basic features are now identified [1–3]. These modes of action have also been studied indoor in the case of industrial constructions involving acidic environments [4,5]. These mechanisms, including heterogeneous reactions, ion substitution, mass loss, diffusion of solution in pores, strain, porosity evolution, leaching, etc. are complex, interact with each other, and lead to a loss of strength and stiffness of the material.

The investigation of acid attack on cement-based materials has been performed either with field measurements in urban areas [6,7],

or with laboratory measurements. The latter have used either simulated acid rain solutions [7–9], or concentrated acid aqueous solutions [10], in order to accelerate the reactions. Sometimes, different reagents are tested simultaneously or alternatively [4,10]. In the course of these studies, three parameters are generally evaluated: the chemical composition of the runoff solution, the change of mass or size of the samples, and their strength decrease. Due to the complexity of the phenomenon, a quantity is generally not measured, although being the fundamental parameter of chemical kinetics: the reaction rate.

Up to now, models of degradation of concrete under acid attack use empirical dissolution laws [11]. We think that the knowledge of well-defined reaction parameters may help in the elaboration of the predicting tools of acid corrosion. As the reaction of dissolution is always combined with other phenomena like precipitation, flow of the solution, diffusion of dissolved species, etc. in standard acid attack setups, these experiments are not usable for pure corrosion rate measurement. Therefore we propose in this article an original methodology, using holographic interferometry, to access to the reaction rate of cementitious materials in acid solutions. We provide values of the pure dissolution rate of hardened Portland cement in three strong acids – nitric, sulfuric and hydrochloric acids – at various pH as first examples of measurements.

Our investigation of hydrated cement acid attack follows a non-conventional procedure, focusing on one single step of the phenomenon, namely on the first one, dissolution. Accordingly a comparison of our results with standard studies on the resistance of

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Table 1

Composition (mass %) of the ordinary Portland cement used in the corrosion experiments.

| CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | Na ₂ O | MgO | K ₂ O | SO ₂ |
|------|------------------|--------------------------------|--------------------------------|-------------------|-----|------------------|-----------------|
| 62.7 | 17.7 | 5.5 | 4.1 | 0.4 | 0.8 | 0.7 | 3.7 |

cement-based materials to acid is not directly possible [12]. Indeed these experiments are global ones, including dissolution, precipitation, cracking, volume expansion ... and do not enable to isolate pure dissolution. But we hope that our main results – values of the reaction rates, real value of the pH at the attacked surface, evidence of the tiny influence of the nature of the strong acid – will (i) find verification in standard studies, and (ii) help to model more accurately acid degradation of cementitious materials.

2. Materials and method

2.1. Samples and acidic solutions

We have used in this study ordinary Portland cement (CEM-1), the composition of which is detailed in Table 1. It is made of at least 95% clinker. The cement paste was cast in Petri dishes and cut, after 28 days of curing in a moist environment, in order to obtain parallelepipedic samples of approximate dimensions $5 \times 5 \times 0.5 \text{ mm}^3$. The water over cement ratio was 0.4. The nitric, sulfuric and hydrochloric acid solutions were diluted with pure water to obtain the required pH. These three inorganic acids being strong, the pH is the convenient quantity to indicate the content of aggressive species in solution. All experiments have been carried out at ambient temperature.

2.2. Holographic interferometry

Our final aim is the measurement of a reliable reaction rate of hardened cement in acid solutions. To be unquestionable, the experiments must guarantee that no other phenomenon (convection, precipitation ...) disturbs the measurement, to provide a pure dissolution rate. This implies that, during the acid attack of the samples, we are able (i) to observe the interface where the reaction proceeds, to study the reaction precisely where it occurs, and (ii) to access to the concentration field in the liquid soaking the solid, in order to detect all possible mass transport phenomena (diffusion, convection) and remove their contribution from the reaction rate. To achieve these two goals, we have carried out real-time digital holographic interferometry measurements.

Here we take advantage of the potentiality of holography to record phase objects, i.e., transparent objects exhibiting only variation of their index of refraction in our case. Here the investigated transparent object is the solution where the solid dissolves, contained in a transparent cell of dimensions $10 \times 10 \times 40 \text{ mm}^3$ (Fig. 1).

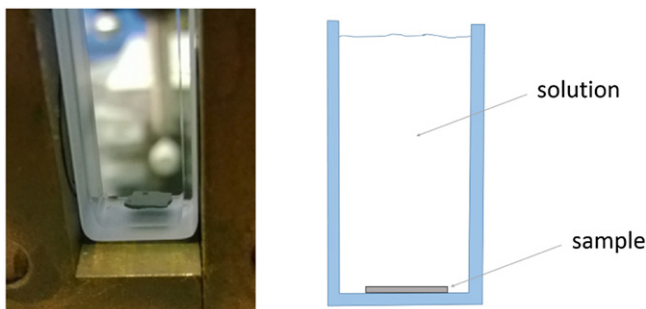


Fig. 1. Photograph and diagram of the experimental cell, containing the acid solution and the hardened cement sample at the bottom.

We record first the state of this corrosive liquid in a so-called reference digital hologram at time t_0 . Here, we choose for t_0 the moment just before the solid is introduced in the cell. Then the hardened cement thin sample is placed at the bottom of the cell. Subsequently we record periodically the digital hologram of the liquid during the attack of the solid. Afterwards we perform numerically a superposition of the holograms at time t_0 and at the various times t to obtain interferograms of the evolution of the state of the liquid between times t_0 and t (Fig. 2). The evolution of the concentration c in the solution, due to the ion release stemming from the attack, induces a change of the refractive index, hence of the phase of the liquid, which is visualized through interference fringes. We want to emphasize that holographic interferometry differentiates from classical interferometry in the fact that no external reference is needed, the object interfering virtually with a memory of itself [13].

A numerical procedure enables to reconstruct the two-dimensional concentration field in the liquid from the fringes (Fig. 3). As only concentration changes inside the cell here, and the concentration was initially uniform, interference fringes are iso-concentration curves. The fringes have always been observed horizontal, so we can deduce that concentration is horizontally invariant, and the evolution is only one-dimensional, in the vertical direction.

The chemical reaction is considered first-order, with the dissolution flux at the interface writing $J = ks_r(1 - c/s)$ with k the reaction rate constant, s_r the reactive surface area, c the concentration of the dissolved species and s their solubility limit. The two physico-chemical quantities s and k both depend on the thermodynamic conditions, the sole varying parameter of which here is the pH. The reaction rate J can be viewed as the velocity with which the concentration curve at the interface $z = 0$ shifts upward (Fig. 3).

The solution of Fick's second law with this chemical reaction at the solid-liquid interface, in a semi-infinite one-dimensional approximation, brings the theoretical concentration evolution $c(z, t)$ with vertical dimension z and time t in the cell:

$$c(z, t) = s \left[\operatorname{erfc} \left(\frac{z}{2\sqrt{Dt}} \right) - \exp \left[\frac{k(s_r/s_d)z}{D\rho s} + \left(\frac{k(s_r/s_d)}{D\rho s} \right)^2 Dt \right] \times \operatorname{erfc} \left[\frac{z}{2\sqrt{Dt}} + \frac{k(s_r/s_d)}{D\rho s} \sqrt{Dt} \right] \right] \quad (1)$$

with s_d the section of the experimental cell, ρ the density of the solution, and D the diffusion coefficient of the dissolved species. The best fit of the experimental curves deduced from the holographic results with the analytic expression of $c(z, t)$ brings the pure surface reaction rate constant k , the solubility of the dissolved species s , and their mean diffusion coefficient D (Fig. 3).

We stress on the fact that the solubility s measured here is the saturation concentration of the dissolving components of hardened cement (see Section 3 for the nature of these components). This solubility has no link with the components precipitating later in the course of the experiment.

Details on the experimental device and data analysis have been given elsewhere, applied to the situation of gypsum dissolution in water [14] and in various aqueous solutions [15].

This method of investigation of hydrated cement corrosion by acid solutions brings the following advantages:

1. The observation of the two-dimensional concentration field in the liquid enables to state that the mass transport of the dissolved species in our quiescent liquid is exclusively diffusional, thereby validating the use of Fick's law to determine the theoretical concentration profile. Indeed, the presence of any non-diffusive fluxes (natural convection, gravitational instability ...) would have induced a distortion of the interference fringes [16].

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