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Drying-rewetting cycles in ordinary Portland cement mortars investigated by electrical impedance spectroscopy

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HIGHLIGHTS

- Portland cement mortar saturated has two relaxations in its electrical impedance.
- These relaxations represent two different size of pores one of them the gel porosity.
- The drying at low temperature confirms the electric model of two relaxations.
- Drying at 50 °C affects the microstructure of the C-S-H gel.

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ABSTRACT

Changes caused in the porous microstructure of ordinary Portland cement (OPC) mortars were studied using electrical impedance spectroscopy (EIS) and equivalent circuit (EqC). Two successive processes, at 20 °C and 50 °C, consisting of several drying-rewetting cycles, were applied to the mortars. After each cycle, the electrical impedance and the amount of water absorbed were measured. The EIS-EqC methodology allowed to find two distributed impedance relaxations, associated to capillary and gel-C-S-H porosities, respectively. At room temperature any microstructural change was not detected. Nevertheless, at 50 °C two microstructural changes were inferred: 1) the volume of accessible porosity increased (pore coarsening) and 2) the surface of the conductive path through C-S-H gel became more conductive (surface smoothing).

1. Introduction

The physical properties of the pore network in hardened cement-based materials (HCB), such as pastes, mortars and concretes, determine their fundamental engineering properties, such as mechanical strength and durability. The pore network can be characterized by a complex function of its pore size, pore shape, pore surface area, volume fraction of pores, connectivity between pores and water saturation level. In mature HCB materials, the pores that contain non-bound liquid water are classified into three classes of porosity, with decreasing size and with different pore shape: i) capillary porosity (>8 nm in diameter) that includes inter-hydrate spaces 8–20 nm, ii) gel porosity (large pores ≈ 8–4 nm in diameter and small pores ≈ 4–2 nm in diameter) and iii) interlayer porosity (<2 nm in width). Henceforth, gel porosity (GeP) will be the volume of pores associated with the C-S-H gel, whose size is less than 8 nm, and capillary porosity (CaP) will refer to the pores greater than 8 nm.

The transition between percolation and depercolation of CaP (communicated or interrupted by the gel C-S-H, respectively) has implications on water curing, transport properties and the durability response of HCB structures. The relationship between the depercolated state and CaP volume has been studied in several ways [1]. The investigation of removing water from HCB materials through drying-rewetting processes is a method for assessing the durability, and is also a useful approach for characterizing different parameters of the pore structure [2].

The intensity of drying depends on the temperature, ambient relative humidity (RH%) and duration of the process. Each drying intensity affects the porosity down to a certain pore size, but the movement of water in these pores alters the redistribution of water in the pores of smaller sizes [3]. Some important features about water displacement and changes in the porosity of HCB materials, subjected to drying processes, are reported in the literature. The most remarkable results at different temperatures are:

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1. Drying at 60 °C:
   a. the cement paste exhibited a coarsening of capillary porosity (increasing the mean size pore) and a collapse of low-density C-S-H gel [4–6].
   b. for 14 days, the mortar lost the water of capillary and gel porosity, but not that of the interlayer porosity [3].
   c. the mortar removed a large fraction of water from the interlayer porosity, but did not at 40 °C [7].
2. Oven-drying of HCB materials at 105 °C for 24 h was used as a reference method for removing completely the non-bound water [8,9].
3. Drying at room temperature and relative humidity RH > 25% was shown to be a reversible process regards to the water content, because the water in the interlayer pores did not move and the water in gel and capillary pores could return after saturation [10]. Drying at room temperature and RH = 0%, and subsequent re-saturating, made the gel particles closer [11].

Several methods have been used to measure changes in the porosity of HCB materials after drying treatments:

1) H-NMR (nuclear magnetic resonance) can evaluate quantitatively the percentages of remaining water [8]. It is also possible to calculate the ratio surface/volume of pores [12] and the gel pore size [3,7,13].
2) SANS (small-angle neutron scattering) gives a direct measurement of i) total internal surface area accessed by mobile water, ii) volume fractal and iii) surface fractal. The first fractal parameter is associated to the packing of C-S-H gel particles, and the second one can be associated with the roughness of the cement grains [2,5,11].
3) WVSI (water vapour sorption isotherms) allows to relate the mass water content to the RH% conditions and the minimum size of saturated pores [6,9,10,14].
4) MIP (mercury intrusion porosimetry) gives a pore size distribution after a drying process [15–17].
5) EIS (electrical impedance spectroscopy) has been used to evaluate the effect of drying on microstructural changes in HCB materials, but only in a few articles [18,19]. The pore coarsening due to drying treatment was related to the size of the frequency arc in the impedance plot. The presence of an intermediate arc in the impedance plot was associated with the formation of denser phases and new interfacial regions between collapsing C-S-H surfaces. However, quantitative analysis was not performed.

The main advantages of the EIS method are twofold: samples can be measured without previous treatments, and the measurement process is non-destructive and non-invasive. The usefulness of EIS (up to 1 MHz), when applied to saturated HCB materials, is that their response shows the ionic conductivity in the pores, distinguishing between the bulk space and the surface.

During the last 20 years, EIS in the range of 1 Hz–1 MHz has been used in HCB materials in order to relate the electrical macroscopic properties to the microstructure [19–37]. In the following paragraphs a brief review related to the EIS technique and the equivalent electrical circuit (EqC) method, applied to impedance data performed in a two-electrode conductive cell, is presented.

The EqC method is based on the configuration of an electrical circuit with passive electrical elements such as resistance R, capacitor C, and constant phase element Q. These elements are connected in series, in parallel or in other arrangement, in order to fit experimental impedance data to theoretical impedance of the circuit, in the frequency range of the experiment.

The admittance of Q is frequency dependent: $Y(Q) = Y_0 (j \cdot 2\pi \cdot f)^n$, characterized by two parameters Y_0 and n (where f is the frequency and j the complex imaginary unit). This complex admittance has two components:

$$ReY(Q) = Y_0 \omega^n \cdot \cos\left(n\frac{\pi}{2}\right) \quad (1a)$$

$$ImY(Q) = Y_0 \omega^n \cdot \mathrm{sen}\left(n\frac{\pi}{2}\right) \quad (1b)$$

Circuits with three branches in parallel have been proposed [38–41], being represented as ($R_1Q_1[R_2Q_2]$) following the circuit description code (CDC) [42]. This parallel circuit represents three main phases of the material with different types of conductivity (with respect to the applied voltage): resistive (R_1, in phase), capacitive (Q_1, out of phase $n_1 \cdot \pi/2$ rad) and resistive-capacitive in series (R_2Q_2, lagged < $n_2 \cdot \pi/2$ rad). This three-branch circuit has the advantage that allows to identify three different phases of the material and to monitor their evolution. However, its weakness is that other alternative circuits with different number of branches in parallel also allow to explain the bulk electrical conductivity.

Recently, a circuit with two Randles in series: R_s (C_1 [R_1W_1]) (C_2 [R_2W_2]) has been applied [20,36,43,44], being W a Warburg element equivalent to a Q element with n = 1/2.

A general circuit for fitting the experimental data, without the need of a priori assumptions, is a Voigt circuit with a certain number of pairs elements in parallel (RC) connected in series. Any set of impedance data can be fitted to a circuit with sufficient number of (RC) [45–48]. This circuit also serves to: i) check if the experimental data fulfil the Kramers-Kronig relations, ii) obtain the time constant of each (RC) ($\tau = RC$) and iii) estimate continuous distributions with some approximate results [45].

If the material system has continuous impedance relaxations, as it is the case of HCB materials, a series circuit with different pairs of (RQ) elements can be used. Each (RQ) represents a different distributed relaxation of the impedance [46,48]. The characteristic time constant T of the distributed relaxation is defined as [21]:

$$T = (R \cdot Y_0)^{(1/n)} \quad (2)$$

Some researchers found a single relaxation (RQ) in OPC mortars [25,49], and also in cement pastes [50]. Other authors presented two relaxations, (R_1Q_1)(R_2Q_2) in OPC mortars [51,52], and even a single relaxation in series with a resistance has been proposed, R_1(R_2Q_2) [53].

A common feature in these investigations with saturated mortars is the presence of a distributed relaxation (RQ) with an exponent n of Q close to 0.80. This exponent n represents the width of the distributed relaxation in the frequency dimension. The value n = 1 corresponds to a narrow Debye relaxation and a decreasing value of n (from 1 to 0.5) means an increase in the width of the relaxation. The exponent n = 0.80 has been related to: i) the fractal dimension of the C-S-H gel [25,49,50], ii) the ratio of dielectric/conductive components in the admixture that constitutes the C-S-H gel [41,54] and iii) the water confined in nanometer size pores [55]. Whatever its meaning is, a change of n depicts a change in the structure of the gel C-S-H in HCB materials.

The main objective of this paper is to establish the methodology EIS-EqC to assess the changes in microstructure of OPC mortars subjected to several cycles of drying at low intensity conditions (20 °C and 50 °C) and subsequent resaturating.

Given the controversy about the number of relaxations in saturated mortars, and in order to facilitate comparability of future studies, one specific objective of this work aims to demonstrate that electrical conductivity of saturated OPC mortars can be characterised by two impedance relaxations of type (RQ). This physical model is validated with the applicability of the same EqC to all saturated states, the original and the resultant states after the successive drying-rewetting cycles throughout the experiment. The