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Electrochemical Impedance Spectroscopy study on the absorption and evaporation processes in natural stones

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ABSTRACT

Efforts have been made to create new procedures based on Electrochemical Impedance Spectroscopy (EIS) to study several characteristics of cementitious materials with practical interest. Similar approaches can be followed to study other materials, in which the comprehension of their physical, transport-related and durability properties are also needful. Natural stones are one of these materials, wherein such properties play a fundamental role on their performance when in service, in both monumental and non-monumental constructions.

This work aims at presenting a first approach on the application of EIS to study electrolyte absorption and evaporation processes in stones. Stones with different porosities and different fluid-transport behaviors were monitored by EIS using a setup of 4 or 2 electrodes assemblies.

During absorption, EIS spectra presented two distinct responses according to the frequency, a resistive behaviour and a capacitive slope. The evolution of the spectra showed that the absorption process can be accurately monitored in less porous stones, whereas in more porous stones the procedure still requires some improvements.

In what concerns evaporation tests, EIS spectra were more complex, especially for longer periods. At early stages two time constants were poorly detectable, but the evolution of evaporation produced progressive modifications on the spectra and a second time constant became well-resolved, as result of two effects: a gradual loss of contact efficiency and a decrease of moisture within the pores.

In both cases EIS enabled to distinguish between different fluid-transport behaviors and showed to be dependent upon the moisture content within the pores and open porosity of each stone variety.

1. Introduction

Electrochemical impedance spectroscopy (EIS) has been widely used to characterize several types of membranes (coatings, polymers, concrete, mortars, etc.) and to describe their interaction with different environments. In the case of cementitious materials, EIS measurements taken with assemblies using two parallel plate electrodes have been frequently used to study the hardening processes and characteristics of their hardened cement pastes [1–6]. The interpretation of the media response has been very challenging, although, it was found that hydration process could be accurately monitored [2,3] and the dielectric constant determined from the high frequency range EIS response [1,4]. As an alternative to the standard tests, additional efforts have been made to create new EIS-based procedures to study the durability and physical properties of cementitious materials, namely pore structure characterization [7], resistance against chloride uptake [8–10], and diffusion coefficients [11].

On such type of assemblies, the electrodes can either directly contact the sample or be isolated using a dielectric material or an air gap. It was claimed that the direct physical contact promotes double layer and charge transfer phenomena in moist conditions

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and consequently the response at high frequencies is dependent on the type of assembly [5]. Due to the highly capacitive behavior of these insulating materials, at certain frequencies, the non-contacting methods may hinder the response of the system. It has been stated that solid materials reveal two time constants at the frequency range 10 MHz to 100 kHz, one attributed to the solid phase contribution and other to the bulk electrolyte filling the pores [4]. Castela *et al.* [11] performed EIS measurements on concrete coupons with different properties during their saturation and evaporation using two contacting electrodes (saturation) and four electrodes arrangements (drying). In both cases, the degree of moisture inside the porous network was successfully described by the EIS data. Similar approaches and interpretations could be followed in the study of other types of porous materials with very high impedance and insulator characteristics [12–15]. Natural stones (hereafter stones) can be placed within this group of materials. Stones have been used worldwide, since ancient times, for ornamental and structural purposes and the knowledge of its intrinsic characteristics [16,17] as well as the interaction phenomena with different environmental conditions [18,19] have been key research issues. Furthermore, studies that support the development of protection/conservation strategies are often based on the knowledge of transport-related properties and on the modifications induced by functional surface treatments [20,21].

Following the potential of EIS for studying porous construction materials, this technique brings crucial information to understand the interaction of stone with the environment.

This paper describes the first steps on the use of EIS to study and to discriminate different fluid transport behavior in natural stones. In this work three stones, characterized by different porosities and permeability were studied by EIS. Measurements were made during the processes of electrolyte absorption and evaporation in the stones.

Based on the current findings and interpretations, it is expected that EIS will be used as an essential tool to accurately predict important stone properties such as pore size distribution, state of decay, or modifications resulting from protection/conservation treatments.

2. Experimental

2.1. Materials characterization

Three different limestones with the commercial trade names of Rosal AR (RA), Moleanos Classic (MC) and Ataíja Azul (AA) were used in this study.

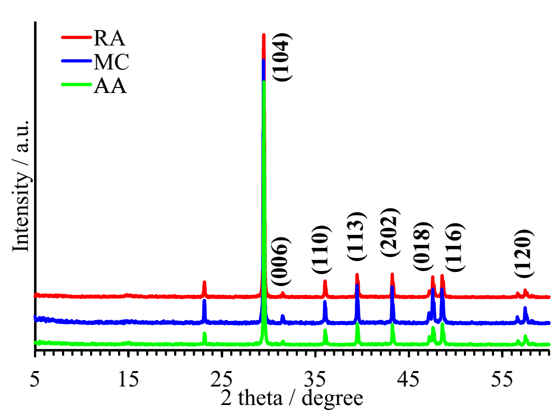

Figure 1. X-ray diffraction spectra of the stones powder samples. The peaks reveal that all stones are mainly composed by calcite.

Table 1
Physical properties of the tested stones (from [16]).

	P_o (%)	A_b (%)	AC ($g/(m^2 s^{1/2})$)	kT ($\times 10^{-16} m^2$)
AA	1.19	0.45	0.36	<0.001
MC	6.54	2.79	16.80	1.200
RA	17.19	7.75	81.62	7.300

The X-ray diffraction patterns (Figure 1) showed that all tested stones are mainly composed by calcite ($CaCO_3$) and that no other major components are present. Therefore, it is expected that the EIS response will be influenced only by the different physical and transport characteristics, which are mainly governed by the non-fissured pore system. The values of open porosity (P_o), water absorption after 48 h of immersion (A_b), capillary water absorption coefficient (AC), and air-permeability (kT) of each limestone variety are summarized in Table 1.

2.2. EIS measurements

All electrochemical measurements were performed in stone slabs of 150x150x10 mm. The absorption tests were carried out using a salt solution with a 1% NaCl and holding the stone slabs between two compartments of a cell (vol.≈0.8L each). The cells used have a four electrode arrangement, with two platinum electrodes at a distance between each other of 5 cm and two stainless steel electrodes working as pseudo-reference electrodes and as counter electrodes, respectively. The area exposed to the electrolyte was 50.12 cm^2.

The measurements started immediately after filling both sides of the cells with electrolyte and were performed until 2 days of exposure. Afterwards, the slabs were removed from the cells and immersed in the same electrolyte to saturate the non-exposed area.

For the measurements under evaporation two electrode cells, composed by two plates of stainless steel (316L) with 100 cm^2 each, were compressed against the stone surface, operating simultaneously as counter and reference electrodes. The measurements were made over time, until spectra stabilization, or until reaching the maximum reading limits of equipment.

The slabs remained in a Faraday cage and at controlled environment of 25 ± 1 °C during the absorption and evaporation tests.

All the EIS measurements were performed by using a Zahner Zennium Electrochemical Workstation and the applied amplitude was 50 mV (rms). Numerical fitting of the impedance data was made using *ZView*® software.

3. Results and Discussion

3.1. Absorption tests

3.1.1. EIS spectra

The EIS measurements during absorption started 4–5 minutes after the first contact of the stone surface with the electrolyte. This period of time corresponds to the complete filling of both cells and electrodes assembly.

Figure 2 exhibits the EIS Bode plots obtained from measurements made during the absorption process. The spectra patterns and their progress over time showed to be dependent on the stone variety.

For the interpretation of the spectra evolution, it is necessary to take into account that the water absorption process in porous materials, as stones, can be divided into two main phases. The first