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In situ electrochemical impedance characterization of cement paste with volcanic ash to examine early stage of hydration

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HIGHLIGHTS

- Electrochemical Impedance Spectroscopy of hydrating cement paste with volcanic ash.
- Particle size and concentration of volcanic ash affect the hydration process.
- EIS is a powerful tool to study free and bound water in hydrating cement pastes.

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ABSTRACT

An experimental investigation using Electrochemical Impedance Spectroscopy (EIS) was carried out when Portland cement was replaced by natural pozzolanic volcanic ash obtained from Saudi Arabia. The cement pastes were sequentially measured with EIS during the early stage of hydration for up to 3 h. Nyquist, Bode and frequency versus phase angle plots were used to evaluate the effect of substitution and particle size of volcanic ash with Portland cement. Warburg impedance was used as a measure to evaluate the chemically bound water during the early part of hydration. This study shows that EIS is a powerful technique for examining the early age water dynamics when naturally available additives such as volcanic ash are used as partial substitutes to Portland cement.

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1. Introduction

Cement paste is a composite mixture of solid, liquid and gaseous components. Additives are used with Ordinary Portland Cements (OPC) to control and engineer cement pastes during the hydration process. The electrical behavior of cement paste to an electric field is a challenging problem given that the micro and pore structure evolution process changes with hydration [1,2]. The cement paste consists of pore fluid which is a solution possessing ionic strength along with a high pH, and is therefore capable of conducting electricity. Electrochemical Impedance Spectroscopy (EIS) is a powerful technique that has been used to analyze the cement pastes, however, limited studies have been performed using EIS for studying the hydration of cement pastes with and without additives [3].

When cement paste is measured under an alternating current (AC) field, the paste exhibits electrical and capacitive responses and can therefore be modeled by the combination of resistors and capacitors. However, the challenge still lies in modeling R-C circuits of a hydrating cement paste as there is significant movement of water during the early stage of hydration. To date, Quasielastic Neutron Scattering [4–8] and Nuclear Magnetic Resonance (NMR) relaxometry [9,10] have been used to track the water dynamics of hydrating cement paste, however, limited studies have been conducted to study the in situ hydration process using EIS.

In 1988, McCarter et al. [11] used impedance spectroscopy to monitor the hydration process after 1, 14 and 25 days of curing. Increase in bulk resistance was detected due to increase in hydration of the cement paste. This study also showed that EIS is effective in studying the capillary and gel pore structure, and presence of water inside capillary pores was detected during the early stage of hydration [11]. Additionally, conductivity of the pore fluid was

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examined and equivalent circuit models were proposed by Scuderi et al. [12] Coverdale et al. [3], Macphee et al. [1] and Cormack et al. [2]. Effect of additives such as silica fume on hydrating Portland cements was studied by Christensen et al. [13] and Gu et al. [14]. These findings showed that impedance measurements were sensitive to changes in hydration kinetics when silica fume was added as a supplementary cementitious material to Portland cement. Additionally, effect of bulk resistance on cement paste was examined by varying the water to cement ratio and silica fume to Portland cement dosages. With the standardization of the equivalent circuit models, EIS was used as a measure for examining the durability of concrete. A recent review article by Hu et al. 2016 discussed in detail the equivalent circuit models that were published so far and their applications related to chloride ion permeability, freeze-thaw, creep, carbonation and steel corrosion resistance in cement paste and concrete [15]. However, the complex and heterogeneous nature of cement paste makes it difficult to model the system using one particular model. Therefore EIS data for hydrating cement paste needs to be validated by other techniques such as Neutron and X-ray Scattering techniques, Calorimetry and NMR relaxometry.

The current work uses EIS to examine the water dynamics during the early stage of hydration when Portland cement is substituted with pozzolanic volcanic ash. Two parameters were varied for this study; (1) concentration of volcanic ash was varied from 10 to 50% and (2) the volcanic ash was ground in three different particle sizes and the effect of the particle size was examined when it was mixed with Portland cement during the hydration process. To date, limited data is available for the first two hours of hydration for OPC cement pastes blended with admixture. This work clearly tracks the difference in early age hydration for cement pastes prepared with OPC mixed with volcanic ash.

2. Materials and methods

2.1. Materials

An in situ experimental evaluation was performed with various combinations of Portland Cement with volcanic ashes. Finely ground volcanic ash was procured from Akhal Province Saudi Arabia. Mixes were prepared by substituting 10, 30 and 50% of Portland cement with volcanic ash (See Table 1). Three different particle sizes of the volcanic ash were used for the experiment. For sample nomenclature, we refer to each mix combination based on the percent replacement of OPC with the particle size of the volcanic ash. For example, 10% substitution of Portland cement with volcanic ash of 17 μm was designated as VA1-10, while 10% substitution of Portland cement with 14 μm was assigned as VA2-10, and for 10% substitution of Portland cement with 6 μm was labelled as VA3-10. The samples were prepared as per ASTM C 305 [16]. A constant water to cement ratio of 0.45 was used for all the combinations. This higher water to cement (w/c) ratio was used to allow sufficient water to react with the cement to form hydration products.

Table 1
Mix proportions and samples cured at 7, 28 and 90 days with 0.45 water to cement (w/c) ratio.

Sample ID	Mean diameter of volcanic ash (μm)	Composition (%)	
		OPC (%)	VA (%)
OPC	–	100	0
VA1-10	17	90	10
VA1-20	17	80	20
VA1-30	17	70	30
VA1-50	17	50	50
VA2-10	14	90	10
VA2-20	14	80	20
VA2-30	14	70	30
VA2-50	14	50	50
VA3-10	6	90	10
VA3-20	6	80	20
VA3-30	6	70	30
VA3-50	6	50	50

VA1 = mean diameter of volcanic ash is 17 μm.
VA2 = mean diameter of volcanic ash is 14 μm.
VA3 = mean diameter of volcanic ash is 6 μm.

The chemical composition and loss of ignition (LOI) of the volcanic ash and Portland cement is shown in Table 2.

2.2. Methods

2.2.1. Particle size distribution analysis

Particle size distribution (PSD) was conducted at Micromeretics, Norcross GA on volcanic ash and OPC by suspending them in isopropyl alcohol using a Laser Light Scattering technique with a Micromeritics Saturn DigiSizer 5205. The mean particle size for the three volcanic ashes was found to be 17.14 μm, 14.48 μm, and 6.40 μm as shown in Table 3.

2.2.2. In situ EIS experiment

The cement paste samples were prepared using deionized water and drawn into a syringe-like cylindrical tube (internal diameter of 20 mm and length of 40 mm), and cylindrical graphite disc electrodes were used for this experiment. Three holes were drilled along the surface of the cylindrical tube mold in order to minimize the entrapped air. During casting of the cement paste two electrodes were positioned at a fixed distance of 40 mm on either side of the cylinder. The graphite disc electrodes were glued to a plexiglas disc and stainless steel screws were drilled inside the discs, and alligator clips were used to connect the screws to the reference electrodes on the impedance analyzer (see Fig. 1). The EIS experiment was carried out using a Solartron AC impedance instrument over a frequency ranging from 2 MHz to 0.1 Hz. AC impedance measurement and data acquisition was controlled using Solartron Model 1287 Potentiostat/Galvanostat interfaced with Solartron Model 1260 Frequency Response Analyzer (FRA) to provide sweep frequency measurements. Both instruments were interfaced with a computer for data logging, storage, and analysis. The applied potential amplitude was in the range of (10–100 mV) in the nominal frequency range, but, for some cases between 100 kHz and 10 MHz. The AC impedance test data were obtained at the open circuit potential. The impedance tests were performed using Solartron instruments with a two electrode configuration; the EIS responses were recorded for every 38 s from the initial stage of mixing. All EIS experiments were carried out at fixed temperature of 25 °C.

A standard Warburg impedance circuit was used to measure the free water by indicating free hydrogen diffusion during the hydration process (see Fig. 2A). R_s is the series resistance, C_{dl} is the double layer capacitance, Z_w is the Faradiac impedance which includes the Warburg impedance, and R_{ct} is the charge transfer resistance. It should be noted that C_{dl} refers to the phase element, which is related to the surface fractal morphology and surface reactivity of the cement matrix/electrode and is significantly influenced by the porosity and geometry of the electrode [17]. Thus, Randles circuit can be used to study the hydration behavior of the cement paste.

Cement pate is a heterogeneous mixture and hydration process is complex due to the simultaneous formation of solid, liquid and porous matrix. Rs represents the pore solution of the cement paste, C_{dl} corresponds to the double layer capacitance between the solid part of the cement paste and free/chemically bound water of the