



# Water dynamics in cement paste at early age prepared with pozzolanic volcanic ash and Ordinary Portland Cement using quasielastic neutron scattering



Kunal Kupwade-Patil <sup>a</sup>, Madhusudan Tyagi <sup>b,c</sup>, Craig M. Brown <sup>b,d</sup>, Oral Büyüköztürk <sup>a,\*</sup>

<sup>a</sup> Laboratory for Infrastructure Science and Sustainability (LISS), Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

<sup>b</sup> NIST Center for Neutron Research (NCNR), National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>c</sup> Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

<sup>d</sup> Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

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## ABSTRACT

Early age hydration kinetics of Portland cement with pozzolanic volcanic ash was examined using quasielastic neutron scattering. Volcanic ash consisting of two different particle sizes was used to prepare cement pastes with different ratios of Portland cement to volcanic ash. The concentration of the volcanic ash played a major role in the bound water index and self-diffusion coefficients of hydration water confined in the cement paste. An increase in the particle size of the volcanic ash affected the degree of hydration by allowing more free and mobile water in the gel pores, suggesting that volcanic ash may not have completely reacted during the experimental time frame. This study shows that the particle size along with variation in volcanic ash composition governs the early age hydration process in volcanic ash cements.

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## 1. Introduction

Supplementary cementitious materials such as volcanic ash are used in the cement industry to effectively utilize waste materials in developing durable and engineered cementitious concretes [1,2]. In addition, this helps in reducing the carbon foot-print by lowering the energy consumption along with enhanced environmental benefits and cost reduction. Volcanic ash (VA) is a locally available material that has been historically used as an additive in cementitious materials to create durable and sustainable concretes [3,4]. The Romans took the first initiative for using lime and natural pozzolans to prepare cements that were used to build the Bay of Naples [4,5]. They finely ground the volcanic rocks and mixed the powder with lime and sand to produce mortars of high strength and durability that could survive in brackish environments. However, not all volcanic rocks are effective since only some have sufficient amorphous content to produce a pozzolanic reaction [1,6]. The inclusion of volcanic ash containing a high alumina content leads to the formation of a binder phase known as calcium–alumino–silicate–

hydrate (C–A–S–H) gel, and when carefully used in correct proportions can lead to a high strength concrete material [3,7,8,41].

A variety of surface and bulk characterization techniques have been used to examine the hydration of Portland cement [9]. Hydration in cements is a complex process and in-situ experiments including nuclear magnetic resonance (NMR), small angle neutron/X-ray scattering, and Raman spectroscopy are commonly used to study the hydration mechanism in Portland cements. Although, these techniques are useful in deciphering the morphological and structural details of cementitious gels; the insight into the role of water during hydration cannot be unraveled. There exist a limited number of characterization techniques suitable for tracking the speciation and role of water during hydration. For instance, 1H NMR relaxometry has occasionally been used for over three decades; a recent set of studies by Valori et al. [10] and Muller et al. [11] provide insight into cement pore–water interactions inside the cementitious gels. These studies discuss techniques for measuring water in different pore sizes along with the specific surface area and density of C–S–H hydrates including gel and capillary pores. An additional technique, inelastic neutron scattering (INS) and quasielastic neutron scattering (QENS) have been used to study the early age kinetics and degree of hydration reaction of C<sub>3</sub>S, C<sub>2</sub>S and C–S–H pastes [7,12–14]. Although, both NMR and neutron scattering techniques use bulk-scale analysis and use signals from protons, the timescale of

\* Corresponding author.

E-mail address: [obuyuk@mit.edu](mailto:obuyuk@mit.edu) (O. Büyüköztürk).

measurements with INS and QENS is superior compared to that of NMR. The energy measured using QENS/INS reflects times in pico-second to femto-second ranges, respectively, while NMR data provides timescales in the millisecond range [7].

QENS is a powerful experimental technique to examine the water dynamics of cement paste during the hydration process [7]. As the cement hydrates, the free water interacts chemically and/or physically in the cementitious matrix forming a glue or gel, which leads to an amorphous phase along with certain crystalline products. QENS helps to identify the transition of water from a free or mobile state to an immobile state during the hydration process [15]. The immobile water is encapsulated in the form of chemically bound water inside the calcium–silicate–hydrate (C–S–H) which is the binding gel in the cement matrix system. The immobile water inside the gel pores (2 to ~5 nm) can be constrained or pseudo-bound, but the water at the interlayer is usually chemically bound [16].

Several studies have used QENS to understand the metamorphosis of multiphase mechanisms which evolve during the hydration process of tricalcium silicates (C<sub>3</sub>S) [17–20], Ordinary Portland Cement (OPC) [21] and incorporation of aluminosilicate sources such as fly ash or ground granulated blast furnace slag (GGBFS) in OPC [21–29]. Bulk water present in the cement matrix is associated with free water in capillary pores and large gel pores, whereas the restricted water is attributed to constrained water where the mobility of water is limited, since it is present inside small gel pores. Chemically bound water is related to the “structural water” present in C–S–H which is a hydration product of OPC based system [17]. Because the neutron signal is largely dominated by hydrogen, the observed immobile molecules are mostly representative of the chemically bound water. Details regarding the calculation of the free and constrained water are characterized by a bound-water index (BWI), the definition of which can be found elsewhere [7,13,22], and has been used as an indicator to characterize the early age kinetics of hydrating cementitious systems. Although, to date, limited studies have been performed with supplementary cementitious additives such as the superplasticizer and GGBFS using QENS [24,30], the existing studies using silica fume blend with OPC possesses similarities to volcanic ash additives as both help to densify the matrix and reduce the porosity while increasing the compressive strength of the matrix [3,4,31,32].

Recent experiments on cement paste using QENS examining the reactivity and dynamics of water molecules bound in the C–S–H gel pore were conducted by Li et al. [30], and complementary molecular dynamics (MD) modeling was performed by Hou et al. [33]. This work used MD simulations with reactive force fields to understand the structure, reactivity and dynamics of water molecules confined in the C–S–H gel nanopores (4 to 5 nm in width). The results showed that due to highly reactive C–S–H surface, hydrolytic reactions take place at the solid liquid interface, thus adsorbing water molecules and transforming Si–OH and Ca–OH chemical groups to be infused in the C–S–H gel structure. Additionally, the stable H-bonds are interconnected with Ca–OH and Si–OH groups thus limiting the mobility of the surface water molecules inside the C–S–H gel.

Effect of additives along with the translational and rotational dynamics of water in OPC pastes cured for 7, 14 and 30 days was examined using QENS [30]. A polycarboxylate-based super-plasticizer helped in confining the mobile water in the C–S–H gel pore that led to the reduction in self-diffusion coefficients and mean jump distance of water molecules. Additionally, the additive helped in the early age evolution of the cement pastes thus forming a uniform and homogenous mixture, which was evaluated using BWI and mean jump distance of the water molecules.

The work we present here details the effect of ash particle size and concentration of volcanic ash when volcanic ash is used as a partial substitute to Portland cement. The objective of this research was to examine the water dynamics of hydrating Portland cement by varying the concentration and threshold particle size of volcanic ash using QENS.

## 2. Materials and methods

### 2.1. Raw material characterization

Finely ground volcanic ash was procured from Akhal Province, Saudi Arabia.<sup>1</sup> Volcanic ash was ground into two different particle sizes using a planetary ball mill. Particle size distribution was performed on the volcanic ashes and Portland cement by suspending them in isopropyl alcohol using the laser light scattering technique with a Micromeritics Saturn DigiSizer 5205. The mean particle size of the volcanic ashes of 17.14 μm and 14.48 μm is designated as IP and FA, respectively (refer to Table 1).

The chemical composition of OPC and volcanic ash was measured using X-Ray Fluorescence (XRF) spectroscopy and the results are shown in Table 2. The sum of silicon oxide (SiO<sub>2</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) components for the raw VA is 64.3%, indicating that the material is a Class C type of ash according to ASTM C 618 [34].

### 2.2. Mixing

Initial dry mixing of the VA and OPC was performed using a Daigger vortex-genie 2 mixer (model no. G560) at 335 rad/s (3200 rpm). This mixing helped ensure that ash was uniformly mixed with the Portland cement prior to exposure to de-ionized water. For convention, we labeled each sample based on the mean particle size and corresponding weight percentage of the volcanic ash. Therefore, a sample with 50 wt.% VA with 17.14 μm (IP) and 50 wt.% OPC is referred to as IP-50, while the similar combination prepared with 14.48 μm is referred to as FA-50 (refer to Table 3).

All samples were mixed with a constant water to cement ratio of 0.55 by mass. The samples were mixed near the experiment station and exposed to beam within 2 min of mixing. The cement paste was sandwiched between aluminum foil and pressed against an annular mold to ensure uniform thickness and to give a cylindrical shape.

### 2.3. Neutron scattering experiments

In-situ experiments on cement pastes were conducted at room temperature on the high flux backscattering spectrometer (HFBS) and disk chopper spectrometer (DCS) at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) [35]. The experimental data on HFBS was measured by 16 <sup>3</sup>He detectors, and the corresponding scattering vector, *Q*, lies between values of 0.25 Å<sup>-1</sup> to 1.75 Å<sup>-1</sup>. The energy resolution of HFBS is 0.8 μeV with a dynamic range of ± 16 μeV, which allows the dynamics of water molecules in the time range from 0.1 ns to 4 ns to be measured. The DCS is a general purpose direct geometry time of flight spectrometer, which uses seven synchronized disk choppers spinning at high speed to produce a pulsed mono-energetic neutron beam [36]. Energies of the scattered neutrons are measured by their individual time-of-flight over a fixed distance of 4.01 m. The incident monochromatic neutron wavelength was 9.0 Å (1.01 meV), which results in an energy resolution of full width half maximum (FWHM) of about 20 μeV. The detectors were grouped to obtain a set of five spectra in the *Q* range from 0.31 Å<sup>-1</sup> to 1.22 Å<sup>-1</sup>. A DCS annular sample can of inner diameter of 17.8 mm and height of 110 mm was used for this experiment. The pre-weighed cement paste was sandwiched in a thin aluminum foil, which was then rolled into an annulus having the same inner circumference of the cylindrical sample holder. Sample height was about 90 mm (foil), and we used beam mask of 80 mm × 17.5 mm. The samples were prepared in annular

<sup>1</sup> Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified is necessarily the best available for the purpose.

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