Materials Characterization 136 (2018) 134–143

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

A new approach of quantitatively analyzing water states by neutron scattering in hardened cement paste

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ARTICLE INFO

Keywords:
Neutron scattering
Water states quantification
Hardened cement paste

ABSTRACT

The three-component model is typically used to analyze the quasi-elastic neutron scattering data and study the water dynamics of hydrating cementitious system. Its application to the hardened cement paste is hindered due to the inaccuracy in evaluating free water at normal ambient temperature. This paper presents a novel approach to quantifying the amount of free water through conducting neutron scattering under freeze-thaw cycling. Disk-like cement paste samples were prepared and applied with four freeze-thaw cycles by varying temperatures in the range of 240 K to 300 K. Quasi-elastic neutron scattering data collected before and after the freeze-thaw cycles and elastic neutron scattering data was collected during each cycle. The signal intensity associated with the free water was obtained by combining QENS and ENS data analysis and a mathematical deduction. We introduced the index of the total immobile water to quantitatively demonstrate water content. The fractional change of the immobile water after freeze-thaw cycle was also studied. The significance of this method is that it is not limited to be applied to cement paste system but also compatible with other systems where the amount of free water cannot be accurately quantified by the standard QENS analysis.

1. Introduction

The dynamic behaviors of water state changes under strong confinement have long been a fascinating subject of considerable interest for many disciplines [1,2]. As the most widely used construction material, cement provides a unique system to be studied at different levels of confinements, because the microstructure of the hardened cement paste is manifested at multiple length scales. According to the average size, pores can be categorized as gel pores, capillary pores, and air voids [3,4]. Gel pores are typically several nanometers large. The capillary pores have sizes ranging from less than 10 nm to larger than 10 μm [5] and their shape can be highly irregular. The air voids are the largest pores, which can reach several millimeters. The state of water is related to the size of the pore in which water is confined. Powers and Brownyard [6–8] have identified three states of water in cement pastes. 1. Chemically bound water is non-evaporable water that becomes a constitutive part of hydration products. 2. Physically confined water includes the gel water and the adsorbed water on the pore surface by hydrogen bonds. 3. Free water is the water in the capillary or larger pores with limited surface bounding or confinement.

Bound water and confined water inside and between the C-S-H (calcium-silicate hydrate) particles influence the cement cohesion, ion transport, concrete creep and shrinkage mechanisms [9,10]. At the same time, water in the capillary pores (free water) plays a dominant role in determining transport properties on micro-scale [11]. Thus, studying the dynamic and structural properties of different water states is crucial to improve concrete durability. Quasi-elastic neutron scattering (QENS) provides a direct and nondestructive way to measure the dynamics of hydrogen atoms over a time scale from picosecond to nanosecond and over the length scales of a few angstroms. This is achieved by measuring the energy exchanged by the scattered neutrons within the sample. It has been utilized to characterize the dynamics of different water states in cementitious materials. For example, the water fractional changes and water dynamic during hydration [12–22] have been studied using a three-component model [14,17,23]. Chemically bound water has been described with a delta function; physically confined water has been described with a narrow Lorentzian function; the free water has been described with a broad Lorentzian function. However, this model is not applicable to investigate the dynamics of different water states in cement paste hardened more than 28 days as the dynamics of free water is too fast to be accurately quantified. Studies [15,23,24] have reported the Lorentzian contribution corresponding to the free water is so broad that it is indistinguishable from the background.

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https://doi.org/10.1016/j.matchar.2017.12.016
Received 14 August 2017; Received in revised form 11 December 2017; Accepted 11 December 2017
Available online 13 December 2017
1044-5803/

Noticing that the motion of free water can be slowed down when it is exposed to freeze-thaw cycles, a new method of quantifying different water states and their relative change in hardened cement samples is proposed in this study. This is achieved by combining: (1) a collection of elastic-neutron scattering data throughout the cycling process and QENS data at the beginning and end of cycling, (2) a mathematical deduction of formulas. Although the cement paste samples are used as an example herein, the importance of this method is universal as it would be of significant interest to other material systems where the motion of free water is beyond the time resolution of the QENS instrument.

2. Neutron Scattering Sample Preparation and Experiment Procedure

2.1. Material and Sample Preparation

Two types of cement paste samples were prepared using Lafarge Type I cement and a mixed solution of light water (H_2O) and heavy water (D_2O). Type I cement has the Blaine fineness of 378 m^2/kg and oxide composition of 19.4 wt% SiO_2, 4.9 wt% Al_2O_3, 2.8 wt% Fe_2O_3, 62.8 wt% CaO, 3.7 wt% MgO, 2.6 wt% SO_3, and 0.55 wt% equivalent Na_2O, with 2.4 wt% loss on ignition, and 0.21 wt% insoluble residue. The density of Type I cement is 3.15 g/cm^3. The adjusted Bogue phase compositions can be calculated using ASTM C150 [25], which are 61.7 wt% C_3S, 7.2 wt% C_2S, 8.0 wt% C_3A, and 8.2 wt% C_4AF. Sample I and II were prepared with water-to-cement mass ratio (w/c) of 0.4 and 0.45, respectively. Before mixing the cement paste, a mixed water solution was prepared using D_2O and H_2O with a molar ratio of 1:1. The cement powder and the prepared water solution were mixed according to ASTM C305 [26], and the mixture was poured into a specially designed mold in order to obtain thin disk cement paste samples with 1.0 mm thickness and 25.4 mm diameter. The mold was covered and placed in a humidity- and temperature-controlled room (98% relative humidity and 24 °C curing temperature) for 24 h. After that, the samples were removed from the mold and submerged into water (with the same H_2O to D_2O ratio) for 27 days with a curing temperature of 24 °C. It should be noted that the introduction of D_2O will alter the reaction kinetics and formation process of hydration products due to the isotopic effects, as reported by Mazumder's and his collaborators' research [27–30]. However, for an inverse geometry spectrometer such as high flux backscattering spectrometer (HFBS) in this study, the neutron beam passes through the sample twice during the experiment, which not only reduces the scattering intensity via sample absorption but also causes multiple scattering. Thus, the use of a D_2O/H_2O mixture is required to reduce the multiple scattering effects to study the hardened cement paste sample. The details of isotopic effects on the cement hydration with a mixed solution of H_2O and D_2O are still unclear, especially at the later hydration stages. The hydration dynamics observed from cement with a mixture of H_2O and D_2O is not easily predictable on the basis of the hydration dynamic observed from cement with pure H_2O or D_2O [28]. Due to the lack of conclusive evidence of isotopic effects on the microstructure of cement hydration with H_2O/D_2O mixture at the later stage, an assumption was made for this study that the microstructure of hydration products remains largely the same. This could be further investigated in future.

2.2. Experimental Procedure

Water dynamics in the hardened cement paste during the freeze-thaw cycles were examined using HFBS at the NIST Center for Neutron Research (NCNR) with two different operational modes. QENS measurements were collected at the beginning and end of cycling for a more precise investigation of the bounded water and confined water in the cement paste matrix. Elastic neutron scattering (ENS) measurement [31] was performed to obtain the elastic scattered intensity (i.e. no energy exchange by the scattered neutron within the instrumental resolution, also called fixed window scan) as a function of temperature. This step, which is the essential part of the new method, is designed to quantify the amount of free water in the hardened cement paste sample as the dynamics of free water confined in capillary pores is too fast to be captured at room temperature by current methods. To overcome this, a freezing process is necessary to hinder the motion of free water. The water-ice phase transition temperature is a function of the size of the pore in which water is present. Namely, the more strongly water is constrained, the lower the transition temperature would be. The differential scanning calorimetry (DSC) studies [32–35] have shown that the freezing temperature of water in small gel pores is substantially lower than that in capillary pores. The freezing temperature of water confined in large gel pores is around − 20 °C to − 30 °C, while water confined in capillary pores freezes at around − 10 °C to − 20 °C [36]. The reported corresponding freezing temperatures by different studies have slight discrepancies, because the freezing temperature is influenced by pore structure, pore solution, and cooling rate, which may vary in those studies. Some of these effects were studied and reported in literatures [37,38]. In this study, free water was expected to be completely frozen at 240 K (− 33 °C), which was chosen as the lower boundary for the freezing process.

Before the experiment, the cement paste samples were taken out from the water solution and their surfaces were wiped with a damped paper towel to obtain a saturated surface dry condition. We expected that all the capillary pores were saturated with water after 28-day curing. Samples were wrapped in an aluminum foil and placed in an aluminum sample container sealed with an indium O-ring. The sample container was attached to the sample holder and placed into a top-loading chamber which could control the sample temperature during the freeze-thaw cycles. For the QENS measurement, HFBS was operated with a dynamic range of ± 11 μeV and an energy resolution ΔE (full-width at half maximum) of 0.79 μeV, covering a scattering vector (Q) range from 0.25 $Å^{-1}$ to 1.75 $Å^{-1}$. The sample was oriented at 45° with respect to the incoming beam. For the self-shielding effects, because of the small size of the sample (25.4 mm diameter disk with 1.0 mm thickness), only approximately 5° of the measured scattering range was shadowed by the edge of the sample. This might explain the reduction in total intensity observed at Q = 0.74 $Å^{-1}$ (Fig. 1). As it will be shown later, no significant dependence of the data on Q was observed. The data were analyzed after summing the spectra at all Qs (except for the Bragg peaks), and the results were obtained from the comparison of the same sample with the identical scattering setup. In this case, it is expected that self-shielding effects is negligible for the purpose of the present investigation.

For each sample, QENS measurement was performed for 4 h before the freeze-thaw cycles at 300 K (27 °C). After that, the first freezing process started and the temperature was decreased from 300 K (27 °C) to 240 K (− 33 °C) with a cooling rate of 1 K/min. After 60 min, the sample temperature reached 240 K (− 33 °C), and was kept constant for 30 min to let the cement paste sample freeze.

Then the first thawing process started and the temperature was increased from 240 K (− 33 °C) to 300 K (27 °C) with a heating rate of 1 K/min. Similarly, about 60 min later, the sample temperature reached 300 K (27 °C) and was kept for 30 min to let the sample thaw. This freeze-thaw cycle was performed four times and the temperature-dependent elastic scattering intensity was measured with ENS during these 4 cycles. At last, QENS was performed at 300 K (27 °C) again for 4 h.

3. Quasi-elastic Neutron Scattering Result Analysis

3.1. QENS Analysis Model

QENS techniques provide information on the samples' dynamics through detecting the difference between energy of the incident and the