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# Hydration-dependent dynamics of water in calcium-silicate-hydrate: A QENS study by global model

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This paper is dedicated to Professor Piero Baglioni on the occasion of his 65th birthday in celebration of his long-time friendship with Professor Sow-Hsin Chen who has cherished the happy and productive memory for their almost 30 years of collaboration with over 70 joint papers, many fantastic visits to University of Florence (for SHC) and Prof. Baglioni's visit to MIT, as well as several important international conferences organized by them together, including the International Workshop on *Topics in Application of Scattering Methods to Investigation of Structure and Dynamics of Soft Condensed Matter*, Florence, Italy, Nov. 11–13, 2005, and the International Workshop on *Dynamic Crossover Phenomena in Water and Other Glass-forming Liquids*, Florence, Italy, November 11–13, 2010. I look forward to many more years of productive scientific discussions with Prof. Baglioni! –SHC

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Structural water index
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ABSTRACT

*Hypothesis:* In a saturated cement paste, there are three different types of water: the structural water chemically reacted with cement, the constrained water absorbed to the surface of the pores, and the free water in the center of the pores. Each type has different physicochemical state and unique relation to cement porosity. The different water types have different dynamics which can be detected using quasi-elastic neutron scattering (QENS). Since the porosity of a hardened cement paste is impacted strongly by the water to cement ratio ($w/c$), it should be possible to extract the hydration dependence of the pores by exploiting the dynamical parameters of the confined water.
*Experiments:* Three C–S–H samples with different water levels, 8%, 17% and 30% were measured using QENS. The measurements were carried out in the scattering vector, $Q$, range from 0.5 $\text{Å}^{-1}$ to 1.3 $\text{Å}^{-1}$, and in the temperature interval from 230 K to 280 K. The data were analyzed using a novel global model developed for cement QENS spectra.
*Findings:* The results show that while increasing the water content, the structural water index (*SWI*) decreases and the confining radius, $a$, increases. Both *SWI* and $a$ have a linear relationship with the water content. The Arrhenius plot of the translational relaxation time shows that the constrained water dominates the non-structural water at water contents lower than 17%. The rotational activation energy is smaller for lower water content. The analysis demonstrated that our newly proposed global model is practical and useful for analyzing cement QENS data.

## 1. Introduction

The reactions between Portland cement and water have been studied for more than a hundred years. The hydration of cement is a two-step process called dissolution-precipitation process [1]. The cement minerals are highly soluble and dissolve rapidly at the interface with water [1,2]. Soon after dissolution, the surrounding water becomes supersaturated and precipitation begins. The new precipitated solid phases, called hydration products, are mainly calcium-silicate-hydrate (C—S—H) and Portlandite [3]. Cement hydration is a continuous process by which the cement minerals are replaced by the hydration products. The water that has

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not been reacted with cement remains entrapped in the porosity generated between the newly formed solid matrix. Most mechanical properties of hardened cement are closely related to the pore system which in turn is linked to the hydration process. Among many parameters that affects the final properties of the cement pastes, the water/cement ratio, or "*w*/*c*" is probably one of the most important [4]. Usually, the lower the *w*/*c*, the stronger and more durable the final cement paste since any space occupied by water will end up as porosity if it is not occupied by the hydration products. However, if *w*/*c* is too low the cement paste is difficult to be handled and sometimes the final product could have poor mechanical properties. Therefore, the ideal *w*/*c* depend on many factors and it is very important to correlate the final cement pore system to the chosen *w*/*c*.

In a saturated cement paste, there are three different types of water [5]: the structural water chemically reacted with cement, the constrained water absorbed to the surface of the pores, and the free water that is unaffected by the presence of the cement matrix. The structural water found in the solid matrix is linked to the degree of hydration since its amount is strictly connected to the amount of hydration products. The constrained water found in very small gel pores or at the surface of large gel pores is closely associated with the formation of new hydration products [6]. The free water is of particular interest because its volume is mainly the capillary pore volume which negatively impacts the strength of hardened cement pastes. Thus, each of these three water types has a different physicochemical state and a unique relation to the cement porosity.

Among the techniques for studying cement, quasi-elastic neutron scattering (QENS) is well suited to investigate the pastes in a saturated state [5,7]. The reason is that neutron is highly sensitive to hydrogen. Hydrogen's incoherent scattering cross section is much larger than any other elements present in a typical cement paste. Moreover, high resolution QENS spectrometers are capable to distinguish H-atoms in different states according to their distinct motions. In a QENS spectrum, H-atoms in the hydration products will contribute to the elastic signal whereas quasi-elastic components come from H-atoms in mobile water. Thus, QENS can provide us information about how much water has reacted with cement to form the hydration products and how much has not. To extract all this information, one needs to use a practical model to analyze the QENS spectra measured. Various models have been developed to model cement QENS data [8,9]. These models have been successfully used to study many problems. Recently, we developed a new global model that can analyze a wide scattering vector, *Q*, range and extract information which was not accessible before [7]. Using this model, we successfully analyzed MgO-based cement with different additives. The global model explicitly expressed the *Q* dependence of both elastic and inelastic components and fits all spectra in the sampled *Q* range simultaneously. By doing so, we can accurately extract from the elastic component the value of the structural water index (*SWI*) and the confining radius, *a*. For the quasi-elastic component, we can further investigate the temperature dependence of both translational and rotational relaxation times in an Arrhenius plot. In this paper, we report on the QENS investigation of three synthetic C—S—H samples with different water contents analyzed by our global model. In the next section, we will explain the model in detail.

## 2. Materials and methods

### 2.1. Materials

The sample used in this investigation consists in a synthetic C—S—H (I) phase resembling the C—S—H present in a cured cement paste so that no evolution is expected with time. QENS spectra from C—S—H gels with three different water contents, 8%, 17% and 30% in the temperature range between 230 and 280 K are reanalyzed with our new global model (see Section 2.2.2). The details on the sample preparation can be find in Ref. [10].

### 2.2. Methods

#### 2.2.1. QENS experiment

QENS spectra were obtained using the high-resolution backscattering spectrometer BASIS at ORNL Spallation Neutron Source (SNS). The energy window is chosen from −120 to +120 μeV with a resolution of few μeV. The highest scattering vector sampled was 2 Å$^{-1}$. Further details on the instrument configuration are reported in Ref. [10].

#### 2.2.2. The global model for analysis of QENS spectra

Motions of the H-atom are composed of three components: the translational motion of the center of mass; rotational motion of the atom around the center of mass; and vibrational motion of the atom around its equilibrium position. According to the well-known decoupling approximation, the intermediate scattering function (*ISF*) of the H-atom can be expressed as [11]:

$$F_H(Q,t) = F_V(Q,t)F_T(Q,t)F_R(Q,t) \quad (1)$$

where $F_V(Q,t)$, $F_T(Q,t)$, $F_R(Q,t)$ are *ISFs* for vibrational, translational and rotational motions, respectively. Since the equivalent time scale of observation in a typical QENS spectrum is much longer than the vibrational period of the hydrogen atom, in this long-time limit, the vibrational *ISF* can be effectively reduced to a Debye-Waller factor (*DWF*) [12]:

$$F_V(Q,t) = \exp(-\frac{1}{3}\langle u^2\rangle Q^2) \quad (2)$$

For our QENS experiment, the magnitude of *Q* is less than 1.3 Å$^{-1}$. Since the O—H bond is about 1 Å, the vibrational amplitude of the hydrogen atom around its equilibrium position cannot be larger than 0.1 Å [12,15]. In this case, the *DWF* is nearly unity for all the *Q* range investigated and thus vibrational motion can be neglected.

Particles confined in a restricted space have a specific geometry of motion which can be modeled by a *Q* dependent elastic incoherent structure factor (*EISF*), $p(Q)$. For a typical cement sample, the free diffusion inside a pore dominates the motion geometry. Thus, the *EISF* is identical to the form factor of the confining volume, *V*. Thus, the *EISF* is described as the form factor of a sphere of radius *a* [11,12]:

$$p(Q) = \left[\frac{3j_1(Qa)}{Qa}\right]^2 \quad (3)$$

where $j_1$ is the first order spherical Bessel function. The self-dynamic structure factor can then be modeled as

$$S_s(Q,E) = p(Q)\delta(E) + (1-p(Q))\mathscr{F}(F_T(Q,t)F_R(Q,t)) \quad (4)$$

where $\mathscr{F}$ denotes a time Fourier transform.

The translational dynamics can be described by the relaxing cage model. For long times, the cage begins to relax, and the molecule diffuses away. This process involves coupled motions of many molecules and is described by a stretched exponential function commonly used in confined water studies [13–19]:

$$F_T(Q,t) \approx \exp\left[-\left(\frac{t}{\tau_T}\right)^{\beta}\right] \quad (5)$$

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