

States of Water in Hydrated Cement Paste: Powers and Brownyard Revisited

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Abstract

In a classic set of experiments in the 1940s, T.C. Powers and T.L. Brownyard characterized the states of water in hydrated cement paste using mass change measurement. Recently, this work was replicated using the nondestructive methods of quasi-elastic and inelastic neutron scattering (QENS & INS). These enabled characterization of the states of water molecules using the partition of kinetic energy among translational, rotational and vibrational modes. All the states of water could be measured simultaneously, and it was not necessary to pre-condition the samples to a specific level of dryness. In general the results of Powers and Brownyard were confirmed. In particular, below an RH of approximately 45%, there is no free (capillary) water in the calcium-silicate-hydrate gel. The (gel) water constrained near the surface appears to have a multiple layer structure. The hydration kinetics curves for different water/cement ratios can be simply re-scaled to the same master curve.

1 Introduction

In a classic set of experiments during the 1940s, T.C Powers and P Brownyard investigated the role of water in the microstructure of hydrated Portland cement paste. Their main analytical method was mass change typically measured using a quartz microbalance. These changes were measured either under what they referred to as isothermal conditions as a function of varying relative humidity at fixed temperature or isobaric conditions with constant RH and varying temperature. In modern terms, the isothermal conditions was the adsorption isotherm and the isobaric conditions the thermogravimetric curve.

Based on these data Powers and Brownyard were able to make inferences about the states of water in the sample [1]. They defined "evaporable water" as the mass loss of a sample upon D-drying. "Non-evaporable water" was then measured as the loss on ignition of the D-dried sample at 1000 °C. They also divided the evaporable water into two categories: "gel water" and "capillary water" based on examination of BET adsorption isotherms for a variety of hydrated cement pastes. The former is estimated to be a layer about 4 molecules thick on the surface of the gel

The capillary water is then the remaining water, which would still experience capillary tension. Powers and Brownyard also observed that the BET relationship applied only below an RH of 45%. In other words, below this threshold there is no capillary water, only the surface layers.

For the variation in w/c ratio experiments, Powers and Brownyard found that different cements developed differing surface areas only when the mixes had w/c ratios greater than 45%. Below that value, they all converged to the same curve. Based on this, P&B concluded that a w/c of 40% was a limiting value. Cement mixes with w/c ratios below this did not have enough water to hydrate completely the Portland cement.

One of the major criticisms of this work has been that it used water vapor as the adsorbate, but water itself is part of the gel structure[2]. Hence, the process of D-drying and then measuring the adsorption isotherm alters the surface area being measured. Other independent methods of measuring the surface area such as N₂ adsorption, mercury intrusion porosimetry and small-angle neutron scattering (SANS) have all given surface area values that differ significantly from the water vapor BET measurements and from each other. Thomas et al.[3] have reconciled these results, and concluded that in fact water vapor adsorption significantly underestimated the true surface area.

A major disadvantage of the water vapor adsorption isotherm method is that the actual data consists of weight change measurements. Thus to obtain information about the states of water from these data requires a series of assumptions about the microstructure of the gel and the behavior of the water. It is also necessary to pre-condition the samples to establish an initial reference state. It would be highly desirable to measure the quantities of water in different states directly. Quasi-elastic neutron scattering (QENS) provides such a means. Thus a series of experiments were carried out the NIST Center for Neutron Research to replicate the work of Powers and Brownyard

2 Experimental Approach

Although the intent was to replicate the work of Powers and Brownyard, there were some differences in the experimental approach. Notably QENS was used to quantify the states of water rather than mass change, pure C₃S was used instead of commercial Portland cement powders and the RH variations control was achieved using static rather than the dynamics methods.

2.1 Quasi-elastic Neutron Scattering

The primary variable measured by Powers and Brownyard was mass. The isobaric experiments this was determined in situ by the elongation of a quartz spring. In the isothermal experiments the samples were removed from the chamber and weighed by a conventional chemical balance. The changes in the states of water in the cement pastes were deduced by the differences in mass.

In contrast, QENS is a direct measurement of the motions of water. These motions can be partitioned into translation, rotations of the hydrogen atoms around the oxygen and vibration along the O-H bonds. In the QENS energy spectrum, water that is bound in the C-S-H will appear as a Gaussian-shaped peak centered at the origin, indicating a purely elastic collision. On the other hand, water that is free to translate randomly produces a Lorentzian type peak in the spectrum. This is used to define a boundwater index (BWI) as $B/(A+B)$, where A is proportional to the area of the Gaussian peak, and B is proportional to the Lorentzian peak area[4]. Since neutron scattering involves interactions only with the nucleus and not with the surrounding electrons, confounding effects of chemical bonding are eliminated. Consequently, the fitting of the QENS data did not require any adjustable parameters.

Since its introduction into the field of cement chemistry, QENS has been used to investigate many aspects of the hydration kinetics of Portland cement, including the effects of temperature[4], particle-size distribution[5] and the C_3S - C_2S ratio[6]. This set of experiments was thus designed to extend this knowledge base by investigating the effects of RH[7] and w/c ratio[8].

2.2 C_3S vs Portland Cement

In their experiments. Powers and Brownyard used various commercial Portland cement powders. In contrast this set of experiments used only pure triclinic C_3S powders. The main reason was to avoid confounding effects due to the presence of other hydrous phases in hydrated Portland cement such as ettringite or katoite. However, in both studies the effects being investigated concerned the C-S-H gel, which is produced by mainly the hydration of the C_3S . Moreover, in a previous QENS study the hydration kinetics of C_3S was compared to a white Portland cement, and no differences were observed during the main reaction period[9].

2.3 RH control

To regulate the RH in their adsorption experiments, Powers and Brownyard used an elaborate airstream apparatus which involved equilibrating continuous streams of dry air with dilute sulfuric acid solutions. Their system was set up with multiple air conditioning trains

which enabled the exposure simultaneously of up to eleven sets of paste specimens at different RHs in the same isothermal chamber. The advantage of this approach is that it enables the RH to be set at any desired value.

This research used a simpler method based on equilibration with saturated salt solutions in closed chambers. This limited the possible RH values to a finite set determined by the commonly available soluble salts. However, there were enough to span the RH range from 6% to 100%. The precision of both methods is roughly the same, about ± 0.25 RH units[10].

3. Sample Preparation

3.1 RH Variation

Pure C_3S powder (Blaine specific surface area 235 m^2/kg) obtained from a commercial source was mixed with distilled water to produce a paste with 0.4 water-to-cement (w/c) ratio by mass. The paste was cast in a plastic vial, sealed under nitrogen atmosphere and cured at 20°C for 28 days. The cured cement paste was then crushed to powder in a mortar and dried at relative humidity levels (RH) levels ranging from 6% to 100%. (see Table I). Portions of the hydrated C_3S powder were equilibrated to the various RH levels by sealing them along with the saturated salt solution, in separate vials, under nitrogen atmosphere at room temperature for 3 weeks. Direct measurements of RH showed that the nominal RH inside the storage container was reached within one day.

Table I. Equilibrium RH of Saturated Salt Solutions [11]

Salt	RH %
NaOH	6.0
LiCl	11.3
MgCl	32.8
K_2CO_3	43.2
$Mg(NO_3)_2$	52.9
$NaNO_3$	74.0
NaCl	75.3
KCl	84.3
K_2SO_4	97.3
H_2O	100.0

For the neutron scattering analysis the samples were loaded in teflon-bags, shaped in an annular geometry with the use of aluminum foil and

sealed in cylindrical aluminum sample-holders under nitrogen atmosphere. To avoid multiple scattering problems, the cement paste thickness was kept below 1 mm to minimize multiple scattering. The sample temperature during the measurement was 30 °C. The QENS measurements were performed on the Fermi Chopper Time of Flight (TOF) instrument at the NIST Center for Neutron Research in Gaithersburg, MD. Details of experiments are given in Nemes et al.(2006)[7]

3.2 Water/Cement Ratio Variation

For this series of experiments, the samples consisted of C_3S powders mixed in varying ratios with distilled water. Typically 4g of cement was mixed with the corresponding amount of water to prepare the paste. The samples were mixed in nitrogen filled glove-bag, loaded into teflon bags, rolled into annular shape and immediately mounted in the Fermi TOF instrument as described above. The QENS data was acquired continuously in-situ for 2 days after mixing for most samples and for a few samples measuring up to 3 days. Counting time was 30 minutes per spectrum. Different sets of samples were maintained at specified temperatures, either 20 , 30 or 40 °C, during the measurement period. Details of these experiments are given in Nemes et al. (2007)[8].

4. Results and Discussion

4.1 RH Variation

The QENS data could be resolved into several components[7]. As discussed above there was the expected Gaussian peak representing the water bound into the CH or C-S-H structure. Two Lorentzians could also be resolved. The broader one is associated with the free or capillary water, while the narrower one is represents the motions of water constrained at or near the surface of the gel[9]. This constrained water thus corresponds the gel water of Powers and Brownyard. In addition to these quas-elastic components, which symmetrical about the origin of the energy shift access, two other peakrs not centered on the origin were observed that indicate inelastic scattering. The one at 41 meV has been identified with the CH content [12] and the other one at 6 meV is apparently due to hydrogen bonding in the free water content. Thus it is possible to quantify all the states of water in hydrating C_3S paste with a single QENS spectrum.

Figure 1 shows the constrained and free water content of the C_3S samples as a function of RH, i.e. the adsorption isotherm. The free water content decreases near-linearly with RH. The exact shape of the RH-free-water curve is a function of the pore-size distribution, governed by the Kelvin-equation, since the critical size pores are remained filled at a given

humidity. Above 50% RH the free water content decreases nearly linearly with decreasing humidity, but the constrained water remains unchanged and decreases rapidly below. It is expected that the amount of gel water does not vary at high humidity,

As the desorption process continues, the free water and constrained water curves coincide at around 45% RH. This is consistent with Powers and Brownyard's finding that there is no capillary water below 45% RH. The fact that free water is still apparently detected below this level suggests that the structure of the adsorbed water layer may be more complicated than a simple monolayer. Powers and Brownyard proposed that the adsorbed layer should be about four molecules thick. If there are multiple layers, the outermost would be more loosely bound, and may appear to be free water in the QENS analysis.

Finally, the good agreement between these measurements made on C_3S paste and the Powers and Brownyard measurements made on Portland cement paste indicate that C-S-H structure is very similar despite the significant differences in the starting materials. This universality of the C-S-H gel structure implies that it does not form topochemically on the surface of the solid grains, but rather by a through-solution process. Since this is completely emptied of water below an RH of 45%, no additional information would be obtained by equilibrating the samples with RH lower than this value. This in turn suggests that an appropriate reference state for pre-conditioning cement paste specimens would be to 45% RH. This could be readily accomplished by equilibrating the samples with a saturated solution of potassium carbonate.

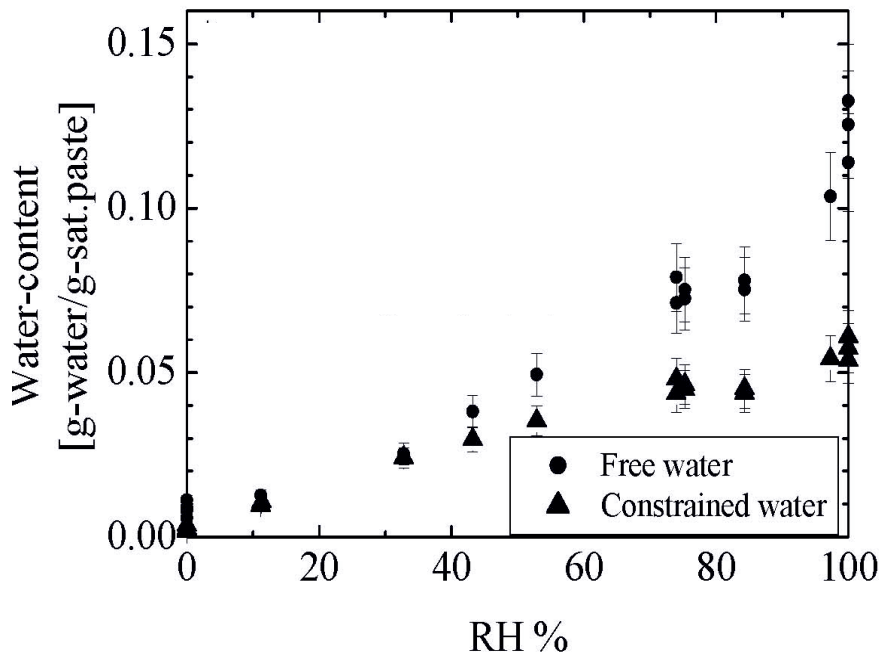


Figure 1: Plot of free and constrained water in cement paste vs RH

4.2 Water/cement ratio variation

This set of experiments measured the time-dependence of the BWI as a function of the w/c ratio. A typical BWI vs time plot is shown in Fig 2. There are two major transitions in the shape of the curve. Point C indicates the approximate end of the induction period and Point D corresponds to t_d , the beginning of the diffusion-limited stage of hydration.

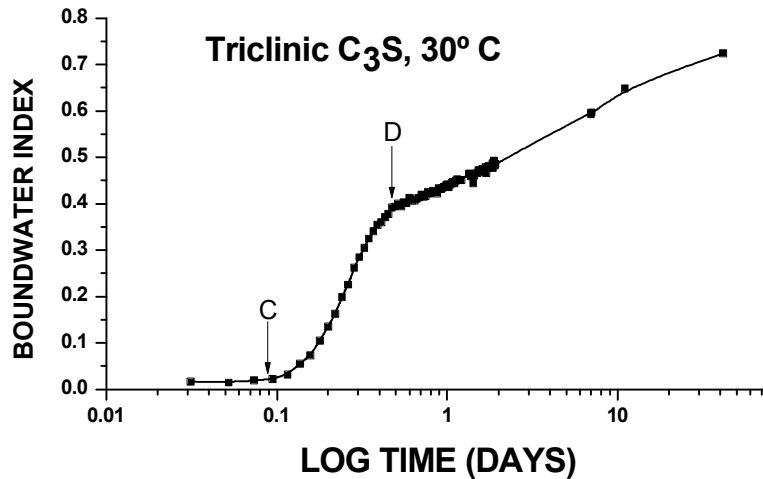


Figure 2: Typical QENS plot of C₃S hydration

In the region between these two points, the BWI increases rapidly. In this rapid nucleation and growth stage, the gel forms in the open pore space surrounding the cement grains. At point D, the gel has filled up all the available pore space, and the hydration reaction can only progress further by water diffusing through the gel to reach the unreacted cement grain surface. During this stage, the BWI curve has a linear relationship with $t^{1/2}$, which is characteristic of a situation of topochemical diffusion with reaction[13].

In the interval between C and D, the gel develops rapidly. The BWI curve at this stage can be fit very successfully with a four parameter exponential model of the form [6]:

$$\beta(t) = \beta(t_0) + A \left\{ 1 - \exp \left\{ - \left[k(t - t_0) \right]^m \right\} \right\} \quad (1)$$

where $\beta(t)$ is the BWI, k is a kinetic rate constant, m is a dimensionality typically 2.65, and A is a parameter related to the nanostructure of the pore-space. This model is shown as the dashed line in Fig. 2. It is very well-known in the materials science literature where it is used to describe nucleation and growth of solid phases. As noted several series of QENS experiments have been conducted to determine how the individual

parameters vary with factors such as temperature[6] and cement particle-size distribution[8]. It was found that A is insensitive to the former but does change with the latter. Presumably, this is because the change in the pore-size distribution affects the intergranular packing and hence the pore-space morphology.

The gel that forms in the period between C and D is associated with outer product. This has different physical properties than the “inner product” that forms in the diffusion-limited stage. It is thought that the outer product contributes more to the strength of the concrete than the latter. Therefore, it would be desirable to maximize the amount this formed by delaying the onset of the diffusion-limited stage.

In Fig 3. the BWI vs time curves of all the pastes hydrated at 30 °C are plotted. The shapes of the curves appear to be similar. In fact, by using a simple scaling factor, the curves can be made to collapse down into a single master curve, as shown in Fig 4. by normalizing to the BWI value at one day of the 40% w/c specimen. This indicates that the main difference among the specimens is the amount of outer product being formed. A similar effect of w/c on the properties of hydrating cement pastes was found by Voight et al.[14]. They found that the curves of ultrasonic reflection of the cement pastes measure as a function time could also be made to collapse to a single master curve.

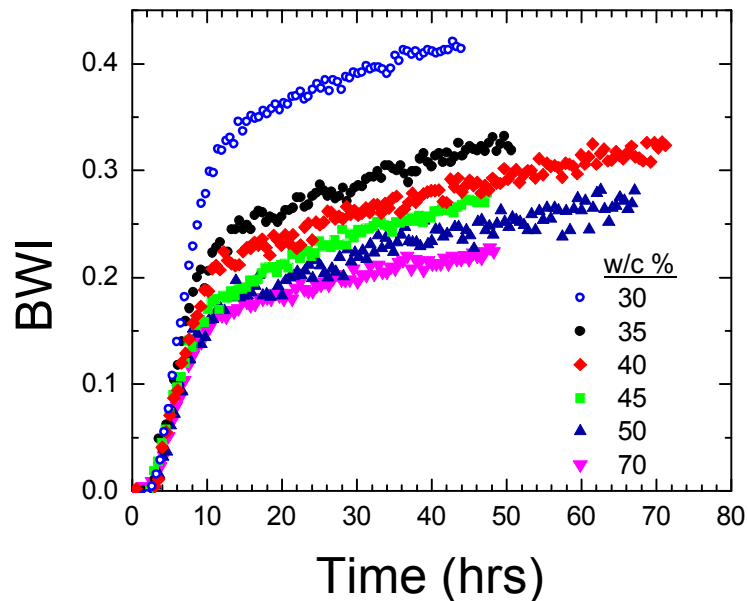


Figure 3: Plots of BWI vs time for all w/c values

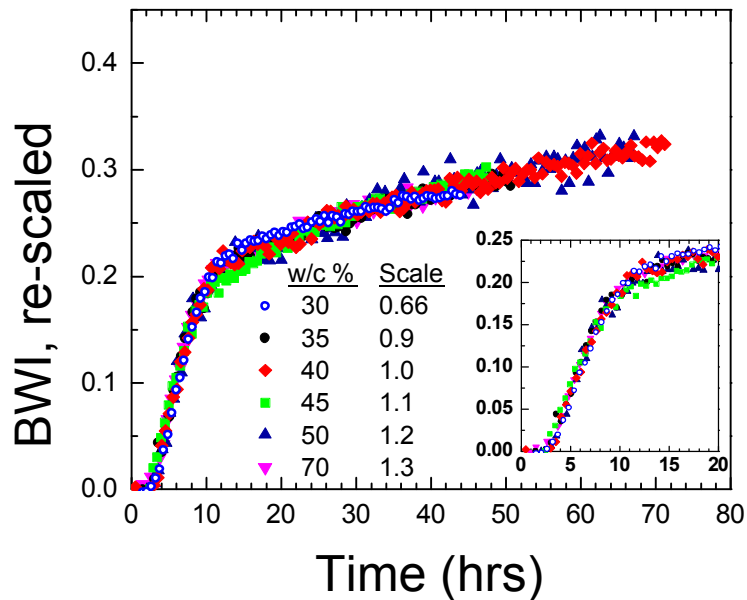


Figure 4: Re-scaled plots of BWI vs time for all w/c values

5. Conclusions

Quasi-elastic neutron scattering has the unique capability of measuring all states of water in hydrated cement paste simultaneously and nondestructively. This consists of the free water (capillary pore water) constrained water (gel water) and bound water (C-S-H and CH). In addition CH content can be determined individually by its inelastic scattering. This makes it possible to re-visit the studies of Powers and Brownyard concerning the effects of RH and w/c ratio on the properties of the C-S-H gel with the advantages of direct measurement of states of water, flexible choice of reference state and nondestructive analysis.

The results confirm the work of Powers and Brownyard. Namely that the capillary pore water decreases nearly linearly with RH, and disappears below a value of 45%. In addition it has shown that pre-conditioning cement pastes with equilibrating them at RH below this causes some loss of gel surface area. Finally, it was discovered that all the hydration kinetics curves produced at different w/c ratios could be made to collapse to a single master curve using a simple normalization procedure.

Future QENS studies of Portland cement hydration will investigate the effects of accelerators and retarders. In addition, the mechanisms of the effect of polymeric additives on the curing process can be studied. Finally, QENS experiments could be used to validate the results of molecular dynamics simulations of the diffusion of water in cement pastes.

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