Hydration of cement: The application of quasielastic and inelastic neutron scattering

Vanessa K. Peterson\textsuperscript{a,b,*}, Dan A. Neumann\textsuperscript{b}, R.A. Livingston\textsuperscript{c}

\textsuperscript{a}NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-8562, USA
\textsuperscript{b}Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, USA
\textsuperscript{c}Federal Highway Administration McLean, VA 22101, USA

Abstract

Quasielastic and inelastic neutron scattering have been highlighted as excellent tools for studying the hydration of cement components. Here, the complimentary application of inelastic and time-resolved quasielastic neutron scattering to investigate the reaction kinetics during the crucial first 24 h of hydration will be highlighted. Some recent results include the interaction of tricalcium and dicalcium silicate during their combined hydration and the effect of the tricalcium silicate crystal form on hydration. The application of these tools for the prediction of strength development in hydrating mixtures is also presented.

\textcopyright 2006 Published by Elsevier B.V.

\textit{PACS:} 78.70.Nx; 81.05.Mh; 82.20.Bc

\textit{Keywords:} Cement; Tricalcium silicate; Quasielastic neutron scattering; Inelastic neutron scattering

1. Introduction

Portland cement is an important construction material, with annual production currently exceeding 800 million metric tones. The structure, molecular composition, and physical properties of cement vary immensely during hydration. The complex details of this metamorphosis depend on both the structure and composition of the starting cement and the hydration conditions. Correlating the original composition and hydration kinetics with the final properties is the aim of this research. With this enhanced understanding, we will improve the ability to design and control the properties of the final product. Neutrons are well suited for the investigation of the hydration of cement, and suggests ways to exploit them to improve cement performance.

Portland cement consists of many components. Tricalcium silicate (Ca\textsubscript{3}SiO\textsubscript{5}—C\textsubscript{3}S) is the most important and abundant, comprising 50–70 wt% of the total. It reacts quickly with water and is the most important component for strength development, particularly in the first 28 d\textsuperscript{[1]}. The hydration of C\textsubscript{3}S is typically written as

\begin{equation}
2\text{Ca}_3\text{SiO}_5 + 7\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O} \\
+ 3\text{Ca(OH)}_2 + 173.6 \text{kJ}.
\end{equation}

Dicalcium silicate (Ca\textsubscript{2}SiO\textsubscript{4}—C\textsubscript{2}S) is the second most abundant component, comprising 15–30 wt% of clinker. C\textsubscript{2}S reacts with water significantly more slowly than C\textsubscript{3}S, contributing little to the strength development in cement at ages less than 28 d. It does, however, contribute substantially to the strength development beyond that time. The hydration of C\textsubscript{2}S is

\begin{equation}
2\text{Ca}_2\text{SiO}_4 + 5\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O} \\
+ \text{Ca(OH)}_2 + 58.6 \text{kJ}
\end{equation}
It has been shown that in a cement paste at 28 d, about 70% of the total C₃S, and about 30% of the total C₂S, have reacted [1]. Compressive strength development is believed to run parallel to the course of the chemical reactions for the hydration of these two phases. Industrially, ordinary portland cement clinkers typically contain a C₃S to C₂S ratio of 3 to 1 [1].

The hydration of C₃S is often used as a model system to study the early stages of the setting process. The hydration of C₃S can be divided into three sections: initial hydrolysis followed by an induction period, nucleation and growth, and diffusion-limited hydration. Initial hydrolysis is the irreversible dissolution of the outer C₃S grain:

\[
\text{Ca}_3\text{SiO}_5(s) + 3\text{H}_2\text{O}(l) \rightarrow 3\text{Ca}^{2+}(aq) + 4\text{OH}^-(aq) + \text{H}_2\text{SiO}_4^{2-}(aq).
\]

This initial hydrolysis period when the C₃S grains rapidly release calcium and hydroxide ions, and a large amount of heat, is short; quickly slowing. The nucleation and growth period begins with the formation of calcium silicate hydrate (CSH) and Ca(OH)₂.

\[
\text{H}_2\text{SiO}_4^{2-}(aq) + x\text{Ca}^{2+}(aq) + (2x - 2)\text{OH}^-(aq) + (y - x)\text{H}_2\text{O}(l) \rightleftharpoons (\text{CaO})_x(\text{SiO}_2) \cdot (\text{H}_2\text{O})_y,
\]

\[
\text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \rightleftharpoons \text{Ca(OH)}_2(s).
\]

As the CSH layer thickens around the unreacted C₃S grains, it becomes increasingly difficult for water molecules to reach the C₃S. The speed of the reaction is now controlled by the rate at which water molecules diffuse through the CSH, known as diffusion-limited hydration. This coating thickens over time, causing the production of CSH to slow. The hydration will continue as long as water and C₃S are present.

As a result of the high sensitivity of neutrons for hydrogen, quasielastic neutron scattering (QENS) and inelastic neutron scattering (INS) can be applied to investigate both the hydration process and local structure of the hydration products that form as a result of these processes. QENS has recently been coupled with hydration models to enable the extraction of a thorough description of the hydration processes occurring in hydrating C₃S [2-13]. This method is reliable, can be performed in-situ, and allows density evaluation of the type of products formed.

The essential step in the hydration of cement components is the transfer of protons from free water to the solution ions, and then to the various end products of the reactions. Thus, one can follow the hydration reaction by determining the state of hydrogen as the reaction progresses. QENS provides a measure of the conversion of free water to structurally/chemically bound water and to water constrained in the pores of the cement paste. In this way, the mechanics of hydration can be probed using the QENS spectra, \( S(Q, \omega) \), which is dominated by the incoherent scattering from hydrogen, as a function of the momentum transfer vector \( Q \) and energy change \( \omega \).

While QENS allows quantification of the combined hydration products, the method does not allow identification of specific quantities of either Ca(OH)₂ or CSH hydration products. The formation of multiple products in hydrating cement further complicates its analysis. INS can be applied complimentary to QENS to allow a separate determination of the hydration products, specifically the amount of Ca(OH)₂ present at any time during hydration of C₃S [4,5,14,15]. Together, these two techniques allow a more complete characterization of the crucial first portion of hydration, allowing the induction, nucleation and growth, and diffusion-limited hydration periods to be examined.

2. Experimental procedure

2.1. Sample preparation

Triclinic and monoclinic C₃S, as well as monoclinic C₂S powders were obtained from Construction Technology Laboratories (CTL, Skokie, IL). Particle size analysis was conducted by CTL. Hydration took place using a water to cement mass ratio of 0.4, at the continuously monitored temperature of 30°C. For QENS experiments, hydration took place inside a sealed Teflon bag inside a rectangular aluminum cell, and for INS experiments samples were sealed in the same Teflon bags and rolled inside an annular aluminum cell.

2.2. QENS measurement

QENS measurements were carried out using the Fermi chopper time-of-flight neutron spectrometer (FCS) [16] at the NIST Center for Neutron Research. The incident neutron wavelength used was 4.8 Å and the sample-to-detector distance was 2.29 m. The calculated elastic scattering energy resolution, \( \Delta E \), was 0.146 MeV. At low values of \( Q \), the width of the quasielastic scattering from the total free water increases quadratically with \( Q \) as expected for Fickian diffusion. At higher \( Q \), the width tends to level off to a more constant value. In view of this and the need to obtain adequate statistics, data were summed over the \( Q \) range of 2.0 to 2.3 Å⁻¹. This produced sufficient statistics, while minimizing the spread in the peak width due to the wide \( Q \) range.

The sample thicknesses were approximately 1 mm in the hydration cell, which was placed at a 45° angle to the incident neutron beam, in reflection geometry. QENS measurements were commenced 30 min after initial mixing.

1Manufacturers are identified in order to provide complete identification of experimental conditions, and such identification is not intended as a recommendation by the University of Maryland, NIST, or the Federal Highway Administration.
and the results were time averaged in 33 min slices. Data were collected continuously up to 55 h.

The profile utility PAN within the data analysis and visualization environment (DAVE) [17] was used for the analyses of QENS data. The QENS spectra were modeled using 3 components:

1. an elastic peak representing completely bound hydrogen using a resolution-limited Gaussian lineshape of width $W_C$ and integrated area $C$, the evolution of $C$ with time has been showed to follow heat evolution for the same hydration [11],

2. the narrowest quasielastic-broadened component arising from pseudo-bound hydrogen using a Lorentzian lineshape of width $W_P$ and integrated area $P$, the evolution of $P$ with time has been shown to track the development of surface area measured using small angle neutron scattering (SANS) [11],

3. a wider quasielastic-broadened component arising from hydrogen in the “free” water was modeled using 2 Lorentzian lineshapes of width $W_{F1}$ and $W_{F2}$.

In all fits, the peak centers were constrained to be the same for each component. $W_C$ was fixed to the width of the resolution function, shown to be a Gaussian function [12]. $W_{F1}$ and $W_{F2}$, were determined from data for the first seven time-averaged slices (3.85 h), where all the water was assumed to be in the free state. These values were fixed for all subsequent fits. For this determination, a Gaussian peak was included to account for contributions to the elastic line arising from the sample and hydration cell. In a similar manner, $W_P$ was determined from the final seven time-averaged slices, and fixed for fits at previous reaction times. All three components were included in these fits. Thus, the number of free parameters included in the fits at each time was reduced to five: the peak centre, and the four integrated areas $C$, $P$, $F_1$ and $F_2$. Fig. 1 shows typical fitting of QENS data using DAVE, and Table 1 lists typical parameter values.

The fits of the individual, time-sliced spectra allowed a time-dependent bound-water index (BWI) to be constructed [10]:

$$
BWI = \frac{C + P}{C + P + (F_1 + F_2)}.
$$

The nucleation, growth, and diffusion limited hydration regimes of the BWI were then fit using the kinetic models that have previously been applied to C3S hydration [2–7].

$$
BWI(t) = BWI(0) + A[1 - \exp{-[k(t - t_i)]^n}](t > t_d),
$$

$$
BWI(t) = BWI(0) + [1 - \{(1 - BWI(t_d))/13\}^{1/3} - (R^{-1})(2D_i)^{1/2}(t - t_d)^{1/2})^{3}\{t > t_d\}.
$$

Here $BW(0)$ is the BWI at the end of the induction period, at the time $t_i$, and $BW(t_d)$ is the BWI at the time diffusion-limited kinetics begins, $t_d$, and $R^{-1}$ is the mean inverse radius of the initial unhydrated particle size, determined from particle size distribution reports sent from CTL. For the mixtures, the $R^{-1}$ corresponding to the dominant phase of the mixture was used. $D_i$ is an effective diffusion coefficient, $k$ the nucleation and growth reaction rate constant, and $A$ the BWI had the nucleation and growth kinetics continued to infinite time. The exponent $n$ has been determined experimentally to be 2.65 at 30 °C for C3S, and this value was used to model QENS data for all mixtures [18]. $t_i$ was established from the QENS hydration plots of $t$ versus BWI$(t)$. $t_d$ was also established from these curves, from the narrow range that resulted in the smooth transition from nucleation and growth to diffusion-limited kinetics in the model. The free parameters in the model were $D_i$, $A$, and $k$, which were fitted to the data in the hydration curves. Fig. 2 shows a typical QENS BWI plot and hydration modeling.

### Table 1

<table>
<thead>
<tr>
<th>Derived integrated area</th>
<th>Full-width at half-max. (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$ (bound $H$)</td>
<td>$W_C = 0.146$ (fixed)</td>
</tr>
<tr>
<td>$P$ (pseudo-bound $H$)</td>
<td>$W_P = 0.4$ (1)</td>
</tr>
<tr>
<td>$F_1$ (Free $H$)</td>
<td>$W_{F1} = 1.22$ (3)</td>
</tr>
<tr>
<td>$F_2$ (Free $H$)</td>
<td>$W_{F2} = 10.5$ (2)</td>
</tr>
</tbody>
</table>

Errors are absolute.

### 2.3. INS measurement

INS data were obtained using the filter analyzer neutron spectrometer (FANS) on BT-4 [19] at the NIST Center for Neutron Research. The sample was oriented, in reflection, at a 45° scattering angle. A Cu (2 2 0) monochromator was used, with pre- and post-collimation of 60° and 40°, respectively. Samples prepared identically to those used...
in the QENS experiment were analyzed, and reflection geometry data only were used. Data were collected over the energy range 25–55 MeV, the range covering the expected peak arising from Ca(OH)2. The reference spectra were measured for a known mass of pure Ca(OH)2 powder placed in an identical experimental set up as the hydrating samples. The sample and reference spectra were obtained under nominally identical conditions to ensure precision in the Ca(OH)2 absolute mass calibration. Measurement of the integrated intensity of the 41 MeV peak enabled the absolute quantity of Ca(OH)2 formed in the hydrated C3S samples to be calculated. Background data consisting of an empty hydration cell were also collected.

The INS spectrum for each sample is representative of the density of states of the sample. DAVE was used for the data reduction and analyses of the INS data. The spectrum for the Ca(OH)2 standard was modeled using 3 Gaussian lineshapes, and a linear background, detailed in Fig. 3. The spectra for the hydrated C3S were modeled using a single Gaussian lineshape and a linear background, due to poorer statistics.

3. Results and discussion

3.1. Interactions of components during hydration

Although it is widely recognized that the hydration of cement involves the interaction of the different components, very little is known about combined reactions. In particular, the less reactive and second most abundant component of cement, was not expected to significantly contribute to the overall hydration in the critical first 24 h. We have undertaken a systematic study of the hydration of controlled mixtures, by wt%, of C3S and C2S. The variation of kinetic parameters of the hydration obtained from the QENS data with composition are shown in Fig. 4. The peak in the parameters makes it apparent that at intermediate compositions the reaction cannot be simply described as a linear combination of the end points as would be the case if the two reactions had proceeded independently.

The parameter \( A \) which represents the expected BWI after infinite time if the nucleation and growth mechanics had not been interrupted, is useful for predicting early strength development, as the amount of product (as well as type) correlates with cement strength. Parameter \( A \) exhibits a maximum for starting mixtures having a mass fraction of 80–95% C3S. The concentration dependence of the effective diffusion constant of water, \( D_i \), which limits the reaction rate in the diffusion-limited regime, correlates well with that observed for the parameter \( A \). \( D_i \) has previously been shown to correlate with the permeability and perhaps the connectivity of the CSH [10]. Finally, the compressive strength (inset in Fig. 4) of mortars based on these mixtures measured after 28 d of hydration also correlates with the QENS results.

In order to quantify the amount of Ca(OH)2 produced during the reaction, INS measurements were performed. The results, displayed in Fig. 5, reveal a clear maximum in the amount of Ca(OH)2 produced at a mass fraction of about 90% C3S.

Taken together, these neutron results demonstrate that the amount of product formed during early hydration times peak for compositions 85–90% C3S. This is particularly surprising for Ca(OH)2 since there is less total Ca in mixtures containing C2S than in C3S alone. Significant changes in \( D_i \) also suggest that the interaction affects the microstructure, and therefore the strength, of the product. Once again, the strengths of mortars of these mixtures cured for 28 d display a peak at 85% C3S.

Hence, QENS and INS shows that a small amount of C2S accelerates the hydration, even though C2S is less reactive than C3S. We attribute this effect to the presence of additional sites for hydration products, provided by the less reactive C2S. This allows the nucleation of CSH to occur at sites remote from the C3S, which is then free to hydrate further. It is postulated that the similar atomic composition and hydration products of the two phases makes the C2S surface favorable as a site for the nucleation.
and growth of products for the hydrating C₃S. It is advantageous to provide these nucleation sites using C₂S rather than inert particles because C₂S not only provides a favorable template, but eventually hydrates itself. Therefore C₂S enhances the later strength of the paste whereas inert particles do not.

3.2. Effect of crystal form on hydration

C₃S exhibits polymorphism, and in cement, it exists as a solid solution of ion stabilized forms. QENS results reveal that monoclinic and triclinic C₃S forms have very different hydration mechanics (Fig. 6). In particular, the rate of product formation during the nucleation and growth regime was found to be higher for monoclinic than for triclinic form. This in turn affects the total amount of product, and therefore differences in the strength in the early stage of hydration may arise. These results are listed in Table 2.

The INS results support these QENS results. Despite having almost half the surface area and marginally less C₃S than the triclinic sample, the monoclinic sample produces almost three times the amount of Ca(OH)₂. Hence, these results agree with the QENS results, which ultimately predicted that more products would be made by the monoclinic sample.

It is speculated that both the crystal form and the type of stabilizing ion entering the lattice affect the type of
products that form during the nucleation and growth regime.

4. Conclusions

QENS and INS have been demonstrated as complimentary tools for the study of the complex hydration of the important and poorly understood calcium silicate phases in cement. This study has shown that the overall hydration reaction of cement is more complex than a simple linear combination of the reactions for the individual components. Thus the hydration reactions do not occur independently in mixtures of C₃S and C₂S, the two crucial components of cement. Unexpectedly, favorable reaction mechanics occur when a mass fraction of 80–95% C₃S mixture is used, where it was previously thought that C₂S played no role during early hydration. Industrial cement clinker contains a mass fraction of approximately 70–80% C₃S out of the total calcium silicate phases, less than the amount determined from this work of 80–95% for optimal hydration mechanics, and strength, at 85%. This suggests that increasing the C₃S content by 5–15% may lead to improved cement. However, there are many other components in cement clinker and other interactions could also affect the performance of the final material.

INS and QENS also reveal a significant effect of crystal form and stabilizing ion on the hydration, indicating that more products would be made by monoclinic C₃S than by the triclinic form. Further work is needed to clarify if this increase translates to an increase in early strength of the paste, and to further explore the effect of stabilizing ions on the hydration.

Finally, the effect of additives on the hydration mechanics and product microstructure is in many cases largely unknown. Traditional methods such as calorimetry lack the sensitivity of the neutron methods presented here that allow the effects of these admixtures to be studied in more detail. QENS has already been applied to observe the effects of an effective retarder (sucrose), and effective accelerator (CaCl₂), to C₃S hydration mechanics [20,21].

Acknowledgements

We thank Craig Brown and Juscelino Leão from the NIST Center for Neutron Research. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.

References

[17] DAVE, National Institute of Standards and Technology Center for Neutron Research.