Inelastic neutron scattering investigation of hydrating tricalcium and dicalcium silicate mixture pastes: $Ca(OH)_2$ formation and evolution of strength

Vanessa K. Peterson[a)]
Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562; and Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742-2115

Dan A. Neumann
Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562

Richard A. Livingston
Federal Highway Administration, McLean, Virginia 22101

(Received 27 January 2006; accepted 20 April 2006)

The hydration of controlled tricalcium and dicalcium silicate mixtures was investigated using inelastic neutron scattering. The amount of $Ca(OH)_2$ produced by each mixture was quantified based on the vibrational mode at approximately 41 meV. The results of compressive strength testing correlate with the amount of $Ca(OH)_2$ produced and with previous results from quasielastic neutron scattering. These results establish a link between hydration mechanics and the evolution of hydration products leading to desirable properties, such as strength.

I. INTRODUCTION

Neutron scattering has been used to study the hydration of both tricalcium silicate and dicalcium silicate individually for some time.[1–9] The high penetration of neutrons and strong scattering from hydrogen makes neutron scattering an excellent technique for the bulk analysis of hydrating cement and its components. Quasielastic neutron scattering (QENS) has only recently revealed that the overall hydration reaction for controlled mixtures of these two components is more complex than a simple linear combination of the individual hydration reactions.[10,11] A maximum for desirable hydration mechanics was identified[10,11] and linked to strength.[10] The weight fraction of tricalcium silicate to total calcium silicate that resulted in this optimization of desirable hydration mechanics and strength of hydrating pastes of tricalcium and dicalcium silicate mixtures, 0.8 to 0.95, was significantly higher than the typical industrial ratio of tricalcium silicate to total calcium silicate, 0.7 to 0.77.[12] This industrial ratio is actually close to a local minimum in hydration mechanics identified using QENS.[10,11]

Previous strength testing used only three replicates of each mixture and failed to reveal the local minimum observed by QENS. The work would be enriched by further strength testing with a greater number of replicates. Additionally, the previous work only approximately quantified the combined hydration products and was unable to identify specific quantities of either $Ca(OH)_2$ or C–S–H produced by each mixture. Unlike QENS, inelastic neutron scattering (INS) can distinguish local environment of the scattering from hydrogen allowing the scattering from $Ca(OH)_2$ to be separated from the other hydrogen contributions.

Here, synthetic mixtures of tricalcium and dicalcium silicates were hydrated, and the average amount of $Ca(OH)_2$ present between 21 and 23 h was determined using INS. Identical mixtures were also prepared, and their 28-day compressive strength was measured, using six sample replicates per mixture. The results, along with those from previous QENS studies, establish a firm link between the evolution of hydration products and desirable properties such as strength.[10,11]

A. Hydration of tricalcium and dicalcium silicate

Ordinary portland cement consists primarily of tricalcium silicate, a component responsible for strength development at early hydration times. Dicalcium silicate is the second most abundant component, and, although it is far less reactive than tricalcium silicate, after 1 year the strengths of pure tricalcium silicate, dicalcium silicate, and cement pastes are comparable.[12] The hydration of

[a)]Address all correspondence to this author.
e-mail: v.peterson@chem.usyd.edu.au
DOI: 10.1557/JMR.2006.0227

tricalcium and dicalcium silicate can be summarized by Eqs. (1) and (2), respectively:

$$2Ca_3SiO_5 + 7H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}4H_2O + 3Ca(OH)_2 + 173.6\ kJ \quad , \tag{1}$$

$$2Ca_2SiO_4 + 5H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}4H_2O + Ca(OH)_2 + 58.6\ kJ \quad . \tag{2}$$

The products from the hydration of dicalcium silicate are the same as those for tricalcium silicate, although the quantitative ratios of the products differ. Calcium silicate hydrate (C–S–H), the first product in the above reactions, is usually amorphous and gives cement its strength; it is generally the phase of interest in cement research.

The hydration reactions can be divided into three processes: initial hydrolysis, nucleation and growth, and diffusion-limited hydration. For the case of the more reactive tricalcium silicate, the hydration proceeds as follows.

The initial hydrolysis (dissolution) is irreversible:

$$Ca_3SiO_5(s) + 3H_2O \rightarrow 3Ca^{2+}(aq) + 4OH^-(aq) + H_2SiO_4^{2-}(aq) \quad . \tag{3}$$

When ion concentrations are sufficient, nucleation and growth of both calcium hydroxide [Eq. (4)] and C–S–H [Eq. (5)] begins:

$$Ca^{2+}(aq) + 2OH^-(aq) \leftrightarrow Ca(OH)_2(s) \quad , \tag{4}$$

$$H_2SiO_4^{2-}(aq) + xCa^{2+}(aq) + (2x-2)OH^-(aq) + (y-x)H_2O(l) \leftrightarrow (CaO)x(SiO^2){\cdot}H_2O \quad . \tag{5}$$

The hydration accelerates as ions precipitate out of solution. As the reaction proceeds, a layer of reaction products forms around the tricalcium silicate grains. This makes it increasingly difficult for water to diffuse though the layer to access unreacted tricalcium silicate, and the hydration reaction becomes diffusion limited. While this greatly slows hydration, the reaction will continue as long as water is present and there are still unhydrated grains.

B. Application of inelastic neutron scattering

INS can be used to determine the amount of $Ca(OH)_2$ present at any time during hydration of tricalcium silicate.[1,8] The application of INS for this purpose involves measuring the energy change in a scattered neutron, which represents the frequencies of the vibrational modes within a sample. The strength of INS lies in the ability to easily calibrate the intensity of the observed peaks to those of a known mass of a chosen reference material. The presence of $Ca(OH)_2$ in hydrating tricalcium silicate can be detected in an INS spectrum at 41 meV due to the oscillation of the hydroxide group. Calibration of the intensity of peak using a standard of pure $Ca(OH)_2$ allows the quantitative determination of $Ca(OH)_2$ in a sample.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

Triclinic tricalcium silicate and monoclinic dicalcium silicate powders were obtained from Construction Technology Laboratories (CTL, Skokie, IL). The same tricalcium and dicalcium silicate used in the previous experiments were used.[10,11] Each sample (as well as mixtures of the two) was hydrated at the continuously monitored temperature of 30 °C using a distilled water to cement ratio of 0.4.

B. Inelastic neutron scattering

INS samples consisted of 60%, 75%, 80%, 85%, 90%, 95%, and 100% mass fraction tricalcium silicate. Hydration took place inside a sealed Teflon bag placed in an annular aluminum hydration cell. INS data were obtained using the National Institute of Standards and Technology (NIST) Center for Neutron Research filter analyzer neutron spectrometer (FANS) at BT-4,[13] using collimations of 60' and 40' before and after, respectively, the Cu (220) monochromator. Data were collected over the energy range of 25–55 meV. The reference spectrum was measured for 3.3057(4) g pure $Ca(OH)_2$ powder placed in an identical setup as the sample and obtained under nominally identical conditions to the sample spectra. Measurement of the integrated intensity of the 41 meV peak as a function of hydration time enabled the absolute quantity of $Ca(OH)_2$ formed in the sample at any time during the hydration to be calculated. A background spectrum consisting of an empty Teflon bag inside a hydration cell was also collected.

The program Data Analysis and Visualization Environment (DAVE)[14] and associated Peak Analysis (PAN) utility were used for the analyses of INS data. Data for the first and last detector (out of 50) were discarded. The background spectrum was subtracted from the sample and reference spectra. The spectrum for the $Ca(OH)_2$ reference was modeled using a linear background and three Gaussian lineshapes, detailed in Fig. 1, while the spectra for the hydrated calcium silicates were modeled using a linear background and a single Gaussian line shape due to the reduced intensity of the peak arising from the contribution to the spectra from the C–S–H. An example of the data fitting to a sample is given in Fig. 2. Any differences between the sample and standard fitting would result in shifts in the absolute quantity of $Ca(OH)_2$ found and not in the trends across the composition range.

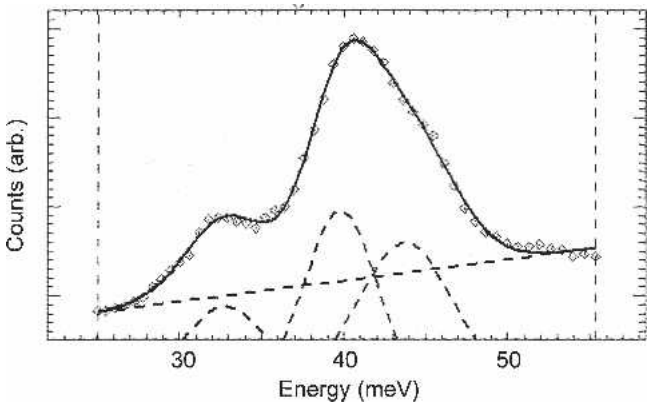

FIG. 1. Inelastic spectra (open diamonds) for the $Ca(OH)_2$ reference and the three Gaussian and background components (dotted lines) used in the DAVE fitting. The bold solid line represents the overall fit.

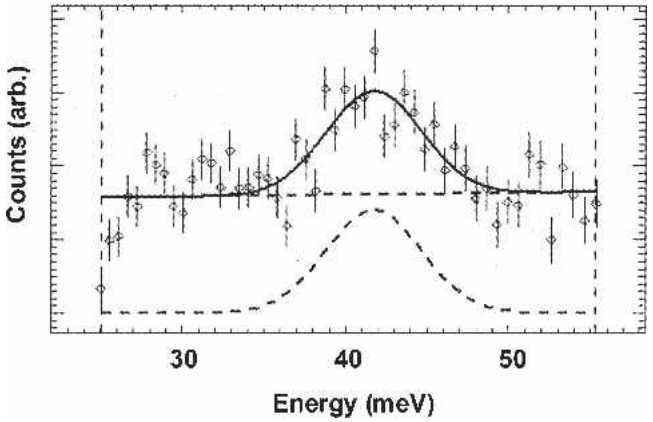

FIG. 2. Inelastic spectra (open diamonds) for the 85% mass fraction tricalcium silicate mixture fitted using Gaussian and background components (dotted line) in DAVE. The bold solid line represents the overall fit.

C. Compressive strength

Compressive strength testing was performed on 1 cubic inch mortars of 50%, 60%, 70%, 75%, 80%, 85%, 90%, 95%, and 100% mass fraction tricalcium silicate mixtures, prepared using C778 graded standard sand from NIST. Samples were cured at 30 °C and contained a cement to water to sand ratio of 1 to 0.4 to 2.75, in accordance with the ASTM C 109 standard, which was followed for the testing.[15] Six replicates of each sample were prepared and tested.

III. RESULTS

A. Inelastic neutron scattering

The quantitative determination of $Ca(OH)_2$ by INS for the various mixtures is shown in Fig. 3. The amount of $Ca(OH)_2$ produced increases with increasing tricalcium silicate content in the mixture, until there is a peak in $Ca(OH)_2$ content, occurring for 85% and 90% tricalcium

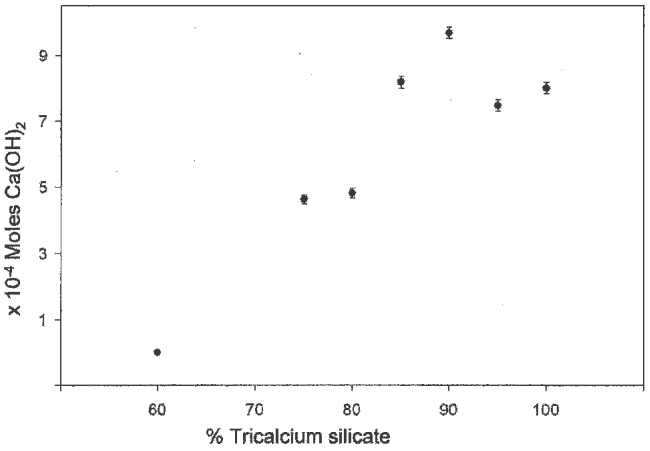

FIG. 3. Amount of $Ca(OH)_2$ in tricalcium and dicalcium silicate mixtures determined using inelastic neutron scattering. Vertical error bars represent one standard deviation in the amount of product, except in the 60% sample, which is reported as 0 without an assigned error. Horizontal error bars represent one standard deviation in composition which is smaller than the data points.

silicate samples. This correlates well with QENS results that displayed a maximum in the amount of bound hydrogen, a measure of the quantity of hydration products, for these same mixtures.[10,11] Thus more hydration products, including $Ca(OH)_2$, are produced during the first day of hydration by mixtures containing 85–95% tricalcium silicate.

A second method of data analysis was also applied to the INS data, taking advantage of the fact that the mixture with the lowest tricalcium silicate content (60%) did not produce any detectable $Ca(OH)_2$ during the first day of hydration. The spectrum for the 60% tricalcium silicate sample, instead of the empty Teflon bag in the hydration cell, was also used as a background spectrum. While using the data for the 60% tricalcium silicate sample as a background spectrum is not entirely justified, due to the potential differences in the C–S–H, application of this data treatment resulted in data that highlighted the $Ca(OH)_2$ peak. This is possibly a result of the subtraction of most of the scattering due to the C–S–H. While C–S–H does not produce a peak in the same region as $Ca(OH)_2$, the increased background obscures the scattering arising from the $Ca(OH)_2$. Qualitatively, this procedure reproduced the trend in the amount of $Ca(OH)_2$ produced by the various mixtures very well. However, the number of moles of $Ca(OH)_2$ calculated from this method was somewhat greater on average than that found using the more conventional method.

B. Compressive strength testing

Figure 4 shows the average, maximum, and minimum compressive strength of the tricalcium and dicalcium silicate mixtures. The spread of these results is significant

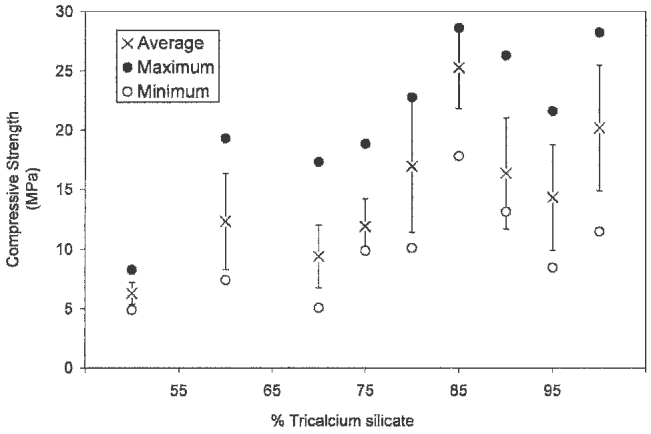

FIG 4. Compressive strength of tricalcium and dicalcium silicate mixtures. Filled circles, crosses, and open circles represent the highest, average, and lowest values, respectively. Error bars represent the average standard deviation from the mean (average) value and are smaller than the points in composition.

for the six tests, although expected, given that considerable variation occurring in compressive strength test results of seemingly identical cement samples is known,[16] particularly as the specimen sizes of this study were scaled down from 2 to 1 in.,[3] and smaller samples have less representative flaw distribution.

The compressive strength increases with increasing amount of the more reactive tricalcium silicate phase. The trend also exhibits two additional features: a maximum at approximately 85% tricalcium silicate and a decrease in the strength between 80% and 70%. The maximum, minimum, and average compressive strength all reflect this trend. These results are consistent with QENS results, which predicted that more product would form in the 80% mixture, and a decrease in the hydration rate and amount of product formed at approximately 70–77.5%.[10,11] Previous compressive strength tests did not include as many compositions in the critical range of 70–85% and so failed to reveal this rapid increase from 70% to the maximum at 85%.[10] It should also be noted that the tricalcium silicate used in these tests did not have the same particle size distribution as used in previous tests and that the mortar samples were packed using a different procedure that ensured a more tightly packed mortar. For these reasons, the strengths obtained here are higher than for previous tests, although the overall trend is consistent.

IV. DISCUSSION

A. Summary of trends

Both the quantity of $Ca(OH)_2$ and the compressive strength of various tricalcium and dicalcium silicate mixtures exhibit similar overall trends. Additionally, previous QENS and compressive strength test results display similar overall trends.[10,11] It should be noted that the compressive strength here and previously was measured after 28 days hydration using different numbers of replicates; the INS data here were measured after 22 h, and QENS data were gathered in situ during the first 50 h hydration. Considering these differences and the difficulties with each of the methods, it is gratifying that the observed trends agree well between the various methods, with only marginal quantitative differences in the composition dependence of the measured quantities. In general, with increasing tricalcium silicate amount, these trends are as follows:

(i) An increase up to compositions with less than approximately 70% tricalcium silicate. This trend can be adequately described by a single mechanism for all results. It appears linear for the amount of $Ca(OH)_2$ produced (INS) and for the rate of product formation (during nucleation and growth kinetics, QENS). It appears parabolic for the permeability of C–S–H (as reflected in the effective diffusion constant measures by QENS) and also for the prediction of the amount of hydration product (that will eventually form, QENS).[10,11] Due to the lack of data and the scatter, the exact nature of the increase cannot be determined for the compressive strength.

(ii) A decrease for compositions containing approximately 70–80% tricalcium silicate. The rate of product formation, type of C–S–H, predicted amount of hydration product, and compressive strength all exhibit a decrease.[10,11] This trend cannot be ascribed to a single reaction mechanism. The trend is less clear for the amount of $Ca(OH)_2$ produced, as determined here, possibly due to the reduced amount of data in this compositional region.

(iii) A rapid increase to an absolute maximum at approximately 80–90% tricalcium silicate. The rate of product formation, type of C–S–H, and prediction of the amount of hydration product all exhibit a sudden, sharp increase and peak at about 85%.[10,11] The results for the compressive strength and for the amount of $Ca(OH)_2$ produced also exhibit their largest values at 85–90%, tricalcium silicate. These maxima cannot be ascribed to a simple superposition of the reactions of the individual components.

(iv) A decrease for compositions from 90% to 100% tricalcium silicate. The permeability of the C–S–H produced and total amount of hydration products both decrease substantially above 90%.[10,11] The decrease is less pronounced for the amount of $Ca(OH)_2$, compressive strength, and the rate of formation of product.[10,11]

B. Hypothesis for the general trend of parameters with increasing quantity of tricalcium silicate

Tricalcium silicate is more reactive with water than dicalcium silicate, and this explains the increased

reactivity of the mixtures with water as the tricalcium silicate content is increased.[10,11]

C. The absolute maximum

During the nucleation and growth regime, Ca^{2+} acts as an accelerant.[17] The replacement of some tricalcium silicate with dicalcium silicate reduces the concentration of Ca^{2+}, thus reducing the reaction rate during the nucleation and growth regime for mixtures less rich in tricalcium silicate. Thus we expected the reaction rate and other hydration parameters to monotonically decrease as one increases the amount of dicalcium silicate in the mixture. However, most of the measurements made to date show extrema at 80–90% tricalcium silicate.

We attribute this absolute maximum in the hydration of tricalcium and dicalcium silicate mixtures to additional nucleation and growth sites provided by the relatively unreactive dicalcium silicate. Although some dissolution of dicalcium silicate is likely to occur, the less reactive dicalcium silicate grains can be considered as sites for nucleation and growth of products. As the hydration products of dicalcium silicate and tricalcium silicate are very similar,[12] the more slowly hydrating dicalcium silicate grains provide a surface that is chemically similar to hydrating tricalcium silicate grains. Dissolution of the outer layers of dicalcium silicate may result in silicate rich sites for nucleation and growth of C–S–H. As the hydration of dicalcium silicate is significantly slower than for tricalcium silicate, the dicalcium silicate surface remains free for nucleation and growth of products from the dissolution of the tricalcium silicate grains. Removal of the ions from solution promotes further dissolution (and hydration) of tricalcium silicate through Le Chatelier's principle. Eventually, the tricalcium silicate grains become occupied with nucleating C–S–H, reducing further dissolution and hydration of tricalcium silicate.

Björnström et al. investigated the accelerating effects of colloidal silica on tricalcium silicate.[18] They attribute the accelerated hydration of tricalcium silicate to an increased number of Si–OH surface groups, which constitute condensation sites for monomeric silica units. The effect was largest during the first 4–12 h. This observation is consistent with the increased reaction rate observed during the nucleation and growth regime of dicalcium silicate and tricalcium silicate mixtures.[10,11] It should be noted although the reaction rate during the nucleation and growth regime increased, the time taken for nucleation and growth to begin decreased linearly with increasing amount of tricalcium silicate. Hence, the dicalcium silicate/colloidal silica was not behaving as a traditional accelerant; it simply promoted hydration once it had begun. These results agree with recent investigations of Lawrence et al.,[19] who identified a higher degree of hydration in mortars containing quartz than for a reference mortar, and also with earlier observations by Yamazaki, who noted that the addition of inert fines assisted the rate of hydration of cement.[20]

During the nucleation and growth period, the hydration layer thickens and acquires the structural attributes that define its permeability. Differences in this local morphology may arise from the faster dissolution of tricalcium silicate, leading to a higher rate of transfer of silicate units to the C–S–H[21] and thus the faster formation of reaction products. However, the permeability of the product layer around the hydrating grains is not only dependent on the rate of product formation but also on its chemical composition. It has been shown that alteration to the Ca to Si ratio alters the structure of the C–S–H layer by changing the ratio of pentamers to dimers of the silicate chains within the structure.[22] As the Ca to Si ratio is reduced, the ratio of pentamers to dimers decreases, and the permeability of the C–S–H increases.

The processes governing the production of the hydration layer define its permeability and are crucial for determining future hydration during the diffusion-limited kinetics, as the amount of reactant that can hydrate is limited by the permeability of the reaction layer. A more permeable layer allows more water to reach the unhydrated portion of the grain, allowing more calcium silicate to hydrate. A decrease in the effective diffusion constant determined from QENS data has been correlated with both the C–S–H morphology and strength.[6,10,11] It was demonstrated that the morphology of the products that formed during an accelerated nucleation and growth regime was more permeable, favoring further hydration.[10,11] Hence, the global maximum in the hydration rate correlates with results for the compressive strength tests and also for the effective diffusion coefficients measured using QENS.

D. Local minimum

Previous QENS work that indicated an interaction of dicalcium and tricalcium silicate during their simultaneous hydration also showed a minimum in the reaction rate and effective diffusion constant just prior to the absolute maximum.[10,11] The compressive strength data here suggest a similar feature. Although the absolute maximum in these parameters can be explained by the presence of dicalcium silicate as an essentially unreactive phase that provides a substrate for nucleation of C–S–H, this minimum in optimal hydration mechanics and compressive strength remains inconsistent with any single mechanism. This local minimum was attributed to an alteration to the Ca to Si ratio in solution and at solid surfaces, resulting from the presence of dicalcium silicate in quantities significant enough to disallow tricalcium silicate from dominating the hydration.

The absence of this minimum in INS results may simply be due to the smaller number of samples in the compositional range of interest relative to the QENS studies.[10,11] Alternatively, quantification of the amount of $Ca(OH)_2$ produced by each mixture is not a direct measure of the degree of hydration for each phase because it does not account for the creation of the C–S–H phase. Hence, it is possible for the overall degree of reaction to be at a minimum, despite the production of more $Ca(OH)_2$. A direct measure of the degree of hydration for these two phases would allow further interpretation of the interaction of dicalcium and tricalcium silicate in this critical compositional region.

V. CONCLUSIONS

INS results demonstrate an absolute maximum in the amount of $Ca(OH)_2$ produced after 22 h by hydrating dicalcium and tricalcium silicate mixtures containing 90% tricalcium silicate. These results correlate with compressive strength tests that also show an absolute maximum. These results are consistent with previous QENS results where a maximum in the rate and the predicted amount of hydration was observed for mixtures containing 80–90% tricalcium silicate.[10,11] Hence, a small amount of dicalcium silicate accelerates the hydration, even though dicalcium silicate is less reactive than tricalcium silicate. We attribute this effect to the presence of additional sites for hydration products that are provided by the less reactive dicalcium silicate. This allows nucleation of C–S–H at sites remote from the tricalcium silicate, which is then free to hydrate further. It was also postulated that the similar atomic composition and hydration products of the two phases makes the dicalcium silicate surface favorable as a site for the nucleation and growth of products for the hydrating tricalcium silicate. It is advantageous to provide these nucleation sites using dicalcium silicate rather than inert particles because dicalcium silicate hydrates at a later time and becomes a significant contributor to the later strength of the paste.

A local minimum in the compressive strength was also identified at mixture compositions containing 70–75% tricalcium silicate, which correlates with a previously observed minimum in the rate and predicted amount of hydration for mixtures containing 75.0–77.5% tricalcium silicate.

Industrial cement clinker contains an approximate ratio of tricalcium silicate to total calcium silicate of 0.70 to 0.77, significantly below the ratio determined from this work of 0.85 to 0.9, for optimal hydration mechanics and strength properties, and within the composition range for the local minimum. There are other interactions between the remaining components in cement clinker left to explore, and it is intended that these will be the subject of future investigations.

ACKNOWLEDGMENTS

Thanks to Juscelino Leão from the NIST Center for Neutron Research for help with INS data collection. Thanks to Dr. Chiara (Clarissa) Ferraris of NIST for help with compressive strength testing.

Manufacturers 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 Federal Highway Administration, nor does it imply that the products are necessarily the best for the purpose.

REFERENCES

1. V.K. Peterson, C.M. Brown, and R.A. Livingston: Quasielastic and inelastic neutron scattering study of the hydration of monoclinic and triclinic tricalcium silicate. *Chem. Phys.* (2006, in press).
2. A. Faraone, E. Fratini, P. Baglioni, and S-H. Chen: Quasielastic and inelastic neutron scattering on hydrated calcium silicate pastes. *J. Chem. Phys.* **121,** 3212 (2004).
3. A.J. Allen, J.C. McLaughlin, D.A. Neumann, and R.A. Livingston: In situ quasi-elastic scattering characterization of particle size effects on the hydration of tricalcium silicate. *J. Mater. Res.* **19,** 3242 (2004).
4. J.J. Thomas, J.J. Chen, A.J. Allen, and H.M. Jennings: Effects of decalcification on the microstructure and surface area of cement and tricalcium silicate pastes. *Cem. Concr. Res.* **34,** 2297 (2004).
5. J.J. Thomas, J.J. Chen, H.M. Jennings, and D.A. Neumann: Ca–OH bonding in the C–S–H gel phase of tricalcium silicate and white portland cement pastes measured by inelastic neutron scattering. *Chem. Mater.* **15,** 3813 (2003).
6. S.A. FitzGerald, J.J. Thomas, D.A. Neumann, and R.A. Livingston: A neutron scattering study of the role of diffusion in the hydration of tricalcium silicate. *Cem. Concr. Res.* **32,** 409 (2002).
7. J.J. Thomas, S.A. FitzGerald, D.A. Neumann, and R.A. Livingston: State of water in hydrating tricalcium silicate and portland cement pastes as measured by quasi-elastic neutron scattering. *J. Am. Ceram. Soc.* **84,** 1811 (2001).
8. S.A. Fitzgerald, D.A. Neumann, J.J. Rush, R.J. Kirkpatrick, X. Cong, and R.A. Livingston: Inelastic neutron scattering study of the hydration of tricalcium silicate. *J. Mater. Res.* **14,** 1160 (1998).
9. J.J. Thomas, H.M. Jennings, and A.J. Allen: The surface area of cement paste as measured by neutron scattering: Evidence for two C–S–H morphologies. *Cem. Concr. Res.* **28,** 897 (1998).
10. V.K. Peterson, D.A. Neumann, and R.A. Livingston: Hydration of tricalcium and dicalcium silicate mixtures studied using quasielastic neutron scattering. *J. Phys. Chem. B* **109,** 14449 (2005).
11. V.K. Peterson, D.A. Neumann, and R.A. Livingston: Interactions of hydrating tricalcium and dicalcium silicate using time-resolved quasielastic neutron scattering, in *Neutron and X-Ray Scattering as Probes of Multiscale Phenomena,* edited by S.R. Bhatia, P.G. Khalifah, D.J. Pochan, and P.G. Radelli (Mater. Res. Soc. Symp. Proc. **840,** Warrendale, PA, 2005), Q2.2, p. 33.
12. H.F.W. Taylor: *Cement Chemistry* (Thomas Telford, London, UK, 1997).
13. T.J. Udovic, D.A. Neumann, J. Leão, and C.M. Brown: Origin and removal of spurious background peaks in vibrational spectra measured by filter-analyzer neutron spectrometers. *Nucl. Instrum. Meth. A* **517,** 189 (2004).

14. DAVE, National Institute of Standards and Technology Center for Neutron Research, Gaithersburgh, MD http://www.ncnr.nist.gov.dave.
15. *Annual Book of ASTM Standards, Section Four: Construction, Designation: C 109/C* (ASTM, West Conshohocken, PA, 2000).
16. R.F. Warner, B.V. Rangan, and A.S. Hall: *Reinforced Concrete* (Longman Cheshire, Melbourne, Australia, 1989).
17. M.C.G. Juenger, P.J.M. Monteiro, E.M. Gartner, and G.P. Denbeaux: A soft x-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydration. *Cem. Concr. Res.* **35,** 19 (2005).
18. J. Björnström, A. Martinelli, A. Matic, L. Börjesson, and I. Panas: Accelerating effects of colloidal nano-silica for beneficial calcium-silicate-hydrate formation in cement. *Chem. Phys. Lett.* **392,** 242 (2004).
19. P. Lawrence, M. Cyr, and E. Ringot: Mineral admixtures in mortars effect of inert materials on short-term hydration. *Cem. Concr. Res.* **33,** 1939 (2003).
20. K. Yamazaki: Fundamental studies on the effects of mineral fines on the workability of concrete. *Trans. Jpn. Soc. Civil Eng.* **85,** 15 (1962).
21. I.G. Richardson: Tobermorite/jennite- and tobermorite/calcium hydroxide-based models for the structure of C–S–H: Applicability to hardened pastes of tricalcium silicate, β-dicalcium silicate, Portland cement, and blends of Portland cement with blast-furnace slag, metakaolin, or silica fume. *Cem. Concr. Res.* **34,** 1733 (2004).
22. A. Nonat: Interactions between chemical evolution (hardening) and physical evolution (setting) in the case of tricalcium silicate. *Mater. Struct.* **27,** 187 (1994).