

# Hydration of Tricalcium Silicate: Effects of CaCl<sub>2</sub> and Sucrose on Reaction Kinetics and Product Formation

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The effects of CaCl<sub>2</sub> and sucrose on the hydration of monoclinic and triclinic tricalcium silicate were studied using quasielastic neutron scattering and calorimetry. Aside from acceleration and retardation, other effects on the reaction were revealed including changes to the rate constant and the type and amount of hydration product. These effects were measured in terms of specific kinetic parameters for the first time. The phenomenon of “delayed acceleration” caused by sucrose is attributed to the solubilization of the silicate species.

## Introduction

Tricalcium silicate (C<sub>3</sub>S) [Ca<sub>3</sub>SiO<sub>5</sub> = C<sub>3</sub>S in cement chemist’s notation, where C = CaO and S = SiO<sub>2</sub>] is the primary component of portland cement and is responsible for early strength development in hydrating cement paste. The hydration of C<sub>3</sub>S can be described by three reaction schemes: initial hydrolysis involving the formation of a C–S–H [C–S–H = calcium silicate hydrate gel, xCaO–ySiO<sub>2</sub>–zH<sub>2</sub>O, where the stoichiometry (x, y, and z) varies, although x:y of C<sub>3</sub>S pastes usually averages 1.75] layer followed by an induction period, nucleation, and growth of Ca(OH)<sub>2</sub> and C–S–H products, and diffusion-limited hydration.<sup>1</sup> Setting, marked by the transition from the fluid to the solid state, begins with the nucleation and growth of products; the time taken for this transition from the fluid to the solid state is called the time to set. Accelerators and retarders can be used to change the time to set of cement. An accelerating admixture is defined as an admixture that accelerates the setting and early strength development of concrete. A retarding admixture is defined as an admixture that retards the setting of concrete. Hence, the accelerating admixture affects both the time to set and the early strength, whereas a retarding admixture only affects the setting time. This means that accelerators are allowed to affect the rate of reaction whereas retarders affect the length of the induction period and their effects on subsequent reaction rates are not specified.<sup>2</sup> CaCl<sub>2</sub> and sucrose are known to be a very strong accelerator and retarder, respectively, although the mechanisms for these effects are not completely understood.

Recent research has suggested that both CaCl<sub>2</sub> and sucrose cause changes to the reaction kinetics, altering the microstructure and morphology of the C–S–H, resulting in alteration of the bulk properties of the material.<sup>3–5</sup> Soft X-ray microscopy was used to observe that the mechanism of product growth during C<sub>3</sub>S hydration proceeded in a similar manner during hydration using a 0.1% mass fraction solution of either CaCl<sub>2</sub> or sucrose.<sup>5,6</sup>

Although CaCl<sub>2</sub> has long been known to accelerate in some way the hydration kinetics, the changes to the kinetic parameters have never been measured. CaCl<sub>2</sub> not only accelerates the setting time but also increases the rate of formation of products and alters the morphology of reaction products that form.<sup>3</sup> The acceleration caused by CaCl<sub>2</sub> is thought to involve Ca<sup>2+</sup> adsorbing to the C<sub>3</sub>S surface, increasing the zeta potential; the smaller ionic size and higher diffusivity of the Cl<sup>–</sup> relative to OH<sup>–</sup> result in an early rupturing of the layer of adsorbed ions.<sup>6</sup> The accelerative power of CaCl<sub>2</sub> has also been attributed to, at least in part, its ability to flocculate hydrophilic colloids such as the C–S–H layer, facilitating diffusion of ions and water through the initial C–S–H layer due to an increased mean pore diameter, allowing a higher rate of diffusion during the early diffusion controlled period.<sup>3</sup>

Aside from retarding the time to set, there are many other effects of sucrose on the hydration reported in the literature, which are not always in agreement. Juenger and Jennings found that sucrose fundamentally changes the microstructure of the hydration products of portland cement and an alteration

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to the hydration processes was implied.<sup>4</sup> Remarkably, sucrose has been reported to increase the rate of reaction once it had begun.<sup>4,5</sup> Odler and Cordes used secondary neutrals mass spectrometry to observe the effects of a 0.7% mass fraction sucrose solution on the hydration of C<sub>3</sub>S in dilute water suspensions; however, they noted only a retardation of the overall hydration with no noticeable effects on the characteristics of the process.<sup>7</sup> There are many theories on the retardation mechanism of sucrose. The early studies on a retardation mechanism of sucrose noted the capability of sucrose to chelate with Ca<sup>2+</sup>,<sup>8,9</sup> concluding from the depression of solution Ca<sup>2+</sup> that the reaction kinetics were being affected,<sup>8</sup> although the solution remains saturated with respect to Ca<sup>2+</sup>.<sup>10</sup> It has been shown that sucrose solubilizes silicate<sup>10–12</sup> and through the preferential sequestration of Ca<sup>2+</sup> may affect the chemistry of the C–S–H precipitation,<sup>13</sup> consistent with the observation of a higher rate and degree of gelation<sup>11</sup> and its description as a “delayed accelerant” due to increased rate of reaction.<sup>4,5</sup> A mechanism for the retardation by sucrose involves the formation of a half-salt that poisons Ca(OH)<sub>2</sub> surfaces and retards the formation of C–S–H by disallowing Ca(OH)<sub>2</sub> as a potential nucleation site.<sup>8,10,11,13,14</sup> Unlike other sugars, sucrose is nonreducing, containing a five-membered ring, and is considered to be intermediate in its ability to form a half-salt with Ca<sup>+</sup>–OH but stable enough not to undergo ring-opening and degradation in alkaline conditions, such as in hydrating C<sub>3</sub>S.<sup>10</sup>

Until recently, most literature research has focused only on the retardation and acceleration effects of these additives and not on the effects on the hydration kinetics; these investigations have been commonly performed on cement and not its individual components. While it is generally accepted that CaCl<sub>2</sub> increases and sucrose decreases in some way the overall hydration of cement, the alterations to hydration kinetics have never been measured. The effects, other than retardation, of sucrose appear varied in the literature, and there are many theories of its mechanism of retardation. This work measures via kinetic parameters and the binding of hydrogen the changes to the hydration kinetics caused by these additives for the first time, and does so using pure C<sub>3</sub>S. The measured changes to the hydration kinetics are discussed in reference to the various literature mechanisms.

Quasielastic neutron scattering (QENS) has been coupled with hydration models to enable the interpretation of the hydration processes occurring in hydrating C<sub>3</sub>S.<sup>15–24</sup> Ap-

plication of hydration models to the data enables information about the reaction kinetics to be quantitatively determined through the derivation of specific kinetics parameters. Furthermore, the permeability of the product microstructure can be inferred. QENS spectra,  $S(Q, \omega)$ , are dependent on the magnitude of the scattering vector,  $Q$ , where  $Q = (4\pi/\lambda)\sin(\theta/2)$ ,  $\theta$  is the scattering angle, and the energy transfer  $= \hbar\omega$ ,  $\hbar = h/2\pi$  ( $h$  is Planck's constant). For the hydration reaction studied here, the incoherent scattering is dominated by that from the hydrogen, present initially in the free water and later in other states within the hydration products. The energy transfer during neutron scattering differs for H in each state.

Most early studies of the effects of accelerators and retarders relied on calorimetry to evaluate the effects of additives on hydration. Calorimetry is a good method for examining the rate of reaction, but cannot provide the depth of information that QENS does, including morphology and quantity of hydration products, making QENS the more powerful tool. QENS measures all H including chemically bound H, less mobile (constrained) H, and free H. The study of the hydration of C<sub>3</sub>S pastes by QENS has been previously compared to data from calorimetry.<sup>22</sup> Calorimetry measures evolved heat and the release of this heat in hydrating C<sub>3</sub>S has been determined to be directly related to the chemical binding of H as measured by QENS; the chemically bound H component (QENS) tracks the heat evolution (calorimetry) closely for the first 2 days.<sup>22</sup> Chemically bound H is associated with the formation of all the Ca(OH)<sub>2</sub> and some of the C–S–H. Constrained H is found in interlayer water in the smallest pores and adsorbed onto surfaces.<sup>22</sup> The constrained H as measured by QENS is associated with the formation of a high surface area C–S–H phase. Evidence for two different C–S–H morphologies has been found: the bound H (H<sub>S</sub>) contributes to a C–S–H phase of structure C<sub>1.7</sub> SH<sub>S1.6</sub>, and the sum of the constrained and bound H (H<sub>T</sub>) contributes to the phase C<sub>1.7</sub> SH<sub>T2.7</sub>.<sup>22</sup> Hence, QENS measures all hydration products and not just those associated with the evolution of heat.

Here QENS is applied to investigate the effects of CaCl<sub>2</sub> and sucrose on the hydration of triclinic and monoclinic C<sub>3</sub>S. Two models, a stretched exponential derived from an Avrami-type rate equation for the nucleation and growth regime and a diffusion-limited growth equation for the later diffusion-limited hydration period, are applied to time-resolved QENS data, allowing a description of the reaction kinetics and product microstructure for each C<sub>3</sub>S and additive. The alterations to the hydration kinetics are quantitatively determined using terms of specific kinetic

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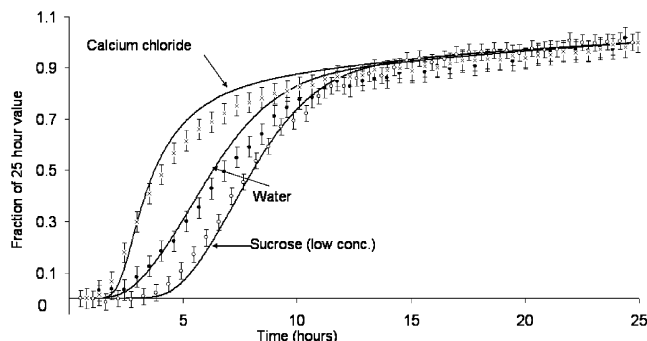
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parameters, rather than simple overall hydration rates. Complementary calorimetry data for the triclinic  $C_3S$  pastes using similarly prepared pastes and additive solutions are also collected and compared to the QENS results. The results are discussed in terms of the current theories for acceleration and retardation mechanisms and hypotheses for the alterations to the hydration kinetics are presented based on extensions of these theories. The literature observation of an accelerated overall hydration caused by sucrose is resolved by this research and a hypothesis for the mechanism presented.

## 2. Experimental Section

**Tricalcium Silicate and Hydration Solutions.** Triclinic and monoclinic  $C_3S$  powders were obtained from Construction Technology Laboratories (CTL, Skokie, IL). [Manufacturers are identified to provide complete identification of experimental conditions, and such identification is not intended as a recommendation by the University of Maryland, NIST, or the University of Texas, nor does it imply that the products are necessarily the best for the purpose.] Particle size analysis was conducted by CTL: the monoclinic sample had an average particle size of  $34\ \mu\text{m}$  and specific surface area of  $0.303\ \text{m}^2\ \text{g}^{-1}$  and the triclinic sample an average particle size of  $10.2\ \mu\text{m}$  and specific surface area of  $0.508\ \text{m}^2\ \text{g}^{-1}$ . Although particle size is known to affect some of the kinetic parameters determined using QENS, production of powders with identical particle size distributions is impossible and the effects are well-characterized.<sup>15,19</sup> 96% pure anhydrous  $\text{CaCl}_2$  was obtained from Acros Organics (Geel, Belgium) and a 4.76(2)% mass fraction solution using distilled water was prepared. Pure sucrose was obtained from Fisher Scientific (USA), and 0.0257(6) and 0.1092-(6)% mass fraction solutions were prepared using distilled water. Each  $C_3S$  form was hydrated at  $30\ ^\circ\text{C}$  using distilled water,  $\text{CaCl}_2$  solution, and the sucrose solutions, using a fluid to component mass ratio of 0.4.

**QENS.** QENS measurements were carried out using the NIST Center for Neutron Research neutron time-of-flight Fermi Chopper Spectrometer (FCS).<sup>24</sup> Hydration took place inside a sealed Teflon bag inside a sealed rectangular aluminum hydration cell. The sample thicknesses were approximately 0.5 mm in the hydration cell, which was placed at a  $45^\circ$  angle to the incident neutron beam. Each energy-transfer spectrum is derived from measurement of the time-of-flight distribution for scattered neutrons arriving at the instrument detectors after each incident neutron pulse. Reflection data were used and summed from several detectors corresponding to the scattering vector ( $Q$ ) range  $2.0\text{--}2.3\ \text{\AA}^{-1}$ . QENS data collection commenced approximately 30 min after initial mixing. Data were collected continuously for up to 55 h and time-averaged over 33 min intervals. The incident neutron wavelength used was  $4.8\ \text{\AA}$ . The energy resolution at the elastic line,  $\Delta E$ , is  $0.146\ \text{meV}$ . The kinetics of the hydration reaction were characterized using the “bound water index” (BWI), which represents the ratio of less mobile (bound and constrained) H relative to the total H in the system. As H is initially only present in the water and is transferred to the reaction products during the hydration of  $C_3S$ , the BWI is essentially representative of the amount of product and was derived with respect to regular time intervals during the course of hydration. With use of the BWI, one model was applied for the nucleation and growth regime and another for the diffusion-limited growth regime, enabling the derivation of parameters describing the kinetics of the hydration reactions. These methods of QENS analyses and hydration modeling have been reported elsewhere.<sup>14–18</sup> The kinetic



**Figure 1.** Overlay of the ratio of bonds formed for the first 25 h for triclinic tricalcium silicate pastes hydrated with water,  $\text{CaCl}_2$ , and low concentration of sucrose, measured using QENS (cumulative bound H, shown with relative error bars) and calorimetry (cumulative heat evolution, shown as solid lines).

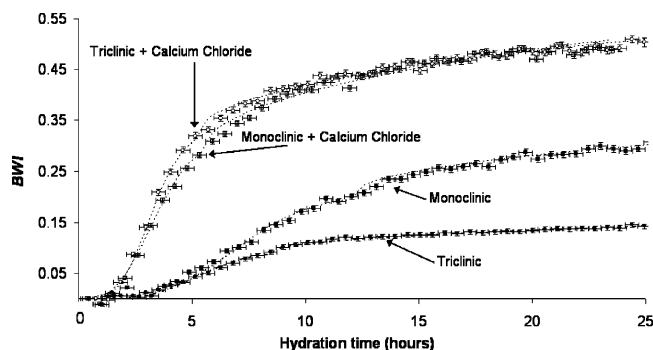
parameters derived from the QENS data include the time taken for nucleation and growth of products to begin,  $t_i$ , the time taken for diffusion-limited kinetics to begin,  $t_d$ , an effective diffusion coefficient,  $D_i$ , the rate constant during nucleation and growth,  $k$ , and the parameter  $A$  representing the expected BWI after infinite time if the nucleation and growth kinetics had not been interrupted. The parameter  $t_i$  is also the time at which setting begins, and the difference between  $t_d$  and  $t_i$  represents the duration of the nucleation and growth regime.  $D_i$  is related to the permeability of the hydration layer around the hydrating  $C_3S$  grains<sup>24</sup> and can be used as an indicator for morphological and microstructural changes to the hydration product. The parameter  $A$  is determined independently of  $D_i$  and is useful for predicting how much hydration will initially occur and correlates with early strength.

**Calorimetry.** Calorimetry measurements were carried out using the TAM Air heat flow calorimeter (Thermometric). Hydration took place at  $30\ ^\circ\text{C}$  inside sealed 20 mL glass ampules using approximately 5–7 g samples. Data were collected continuously for 50 h.

## 3. Results and Discussion

Figure 1 shows that an overlay of the bound H/total H ratio matches the cumulative heat evolved when both are normalized to their maximum for the same time period (shown here for 25 h), for both additives and water. This comparison demonstrates that the QENS data contain the same measured quantities as the calorimetry data and validates further the theory on the different measured quantities of calorimetry and QENS BWI data.<sup>21</sup> Unlike the calorimetry data, the QENS BWI data contain additional information about reaction products that incorporate constrained H, whose formation is not associated with the evolution of heat at this time. As the QENS data allow a quantitative determination of the kinetics through the derivation of kinetic parameters and measure this constrained H component, the QENS data are used to measure the changes to the reaction kinetics, while comparisons between the QENS BWI and calorimetry data are discussed in relation to their general trends of agreement rather than derived kinetic parameters.

Two different crystal forms of tricalcium silicate are used, primarily for the demonstration of the effects of the additives on two forms, and not for comparisons between them. The different behaviors of the monoclinic and triclinic samples have been described elsewhere, although the main finding of this work was that while the monoclinic form has a lower



**Figure 2.** BWI data for triclinic (●, ○) and monoclinic (■, □) tricalcium silicate pastes hydrated using distilled water (closed markers) and CaCl<sub>2</sub> (open markers). Dotted lines indicate the fits of the hydration models to the data. Error bars represent absolute error.

rate constant, it formed more hydration product (that was more permeable) as a result of a longer nucleation and growth period.<sup>15</sup>

**Effects of CaCl<sub>2</sub>.** BWI versus time curves for C<sub>3</sub>S hydrated using distilled water and CaCl<sub>2</sub> are shown in Figure 2; parameters of the reaction kinetics are compared in Table 1.

Calorimetry data were recorded for the same triclinic C<sub>3</sub>S hydrated with the same fluid to component ratio as the samples for the QENS analysis and are shown as cumulative heat evolved with time curves in Figure 3. Calorimetry curves for triclinic C<sub>3</sub>S hydrated using water and a 5% mass fraction CaCl<sub>2</sub> solution display similar trends to the QENS BWI curves for these samples, corroborating the QENS results. The increase in the amount of product measured using BWI (QENS) at the end of the nucleation and growth period for the triclinic C<sub>3</sub>S hydrated in the presence of CaCl<sub>2</sub> appears slightly greater than the increase in heat evolved observed by calorimetry. This reveals the presence of more constrained H, consistent with the formation of a high surface area, lower density C–S–H phase in which the H is less strongly bound,<sup>22</sup> as observed by the accelerated growth of lower density C–S–H.<sup>3</sup>

The BWI curves for the two tricalcium silicates hydrated in the presence of CaCl<sub>2</sub> appear more similar than for those hydrated with water alone. Thus, the addition of CaCl<sub>2</sub> affects the hydration kinetics more strongly than the variations in the crystal form do. The elimination of the differences in crystal form as the controlling factor in the reaction kinetics upon addition of CaCl<sub>2</sub> is a surprising new finding.

As expected, the time for set to begin ( $t_i$ ) is significantly reduced by the addition of CaCl<sub>2</sub>. Additionally, the duration of the nucleation and growth regime ( $t_d$ ) reduces. The rate constant,  $k$ , during nucleation and growth increases upon CaCl<sub>2</sub> addition. CaCl<sub>2</sub> is known to behave as a traditional accelerator by reducing the time for nucleation and growth to begin and thought to accelerate in some way the overall hydration. This result proves that it accelerates the hydration in terms of increasing the rate constant, consistent with the observation of a greater maximum hydration rate achieved using CaCl<sub>2</sub> than water alone.<sup>3,26</sup>

$d(\text{BWI})/dt$  represents the rate of formation of products during the (approximately linear) nucleation and growth section of the BWI curves; addition of CaCl<sub>2</sub> causes a large increase in this value. The  $d(\text{BWI})/dt$  differs from the rate constant,  $k$ , and is dependent on the amount of C<sub>3</sub>S available for hydration and is thus affected by particle size distributions.  $d(\text{BWI})/dt$  reaches a maximum which is proportional to the product  $Akn$ .

The parameter  $D_i$  has been linked to the permeability of the hydration layer.<sup>24</sup>  $D_i$  increases when CaCl<sub>2</sub> is added, indicating that a more permeable product is formed. The alteration to the morphology of the reaction products that form around the hydrating grain caused by the addition of CaCl<sub>2</sub> observed in this study is consistent with the literature.<sup>3,4</sup> These changes may be attributed, but are not limited, to the differences in the chemistry of the systems that affect the rate at which complexes are transferred from solution to the growing particles of C–S–H, postulated to be responsible for a change in product morphology.<sup>27</sup> This is consistent with the observation of an increase in the rate constant,  $k$ .

The addition of CaCl<sub>2</sub> causes an increase in the parameter  $A$ , the theoretical amount of product that would form at infinite time if nucleation and growth processes were not interrupted by diffusion-limited hydration. This effect is attributed to the permeability of the products formed, allowing more product to hydrate in the presence of CaCl<sub>2</sub>. The increased rate constant,  $k$ , is also consistent with the increased amount of product. It should be noted that an increase in the permeability of the hydration product would be expected to result in an increase in the duration of the nucleation and growth regime and the observed reduction is consistent with a large increase in  $k$ , causing faster product accumulation and diffusion-limited hydration to be attained sooner. This result theoretically translates to an increase in early strength of the paste, if changes to the product microstructure and morphology do not compromise its strength. These results agree with a higher observed degree of hydration for C<sub>3</sub>S hydrated with CaCl<sub>2</sub> compared to water.<sup>6</sup>

The acceleration of the overall hydration and time to set of C<sub>3</sub>S induced by CaCl<sub>2</sub> is thought to occur through actions including the adsorption of Ca<sup>2+</sup> to the C<sub>3</sub>S surface, increasing the zeta potential, and the smaller ionic size and higher diffusivity of the Cl<sup>-</sup> relative to OH<sup>-</sup>.<sup>6</sup> The changes in the QENS measured parameters here support this theory and the theory of increased C–S–H flocculation by the CaCl<sub>2</sub>, resulting in increased average pore diameter, allowing faster diffusion.

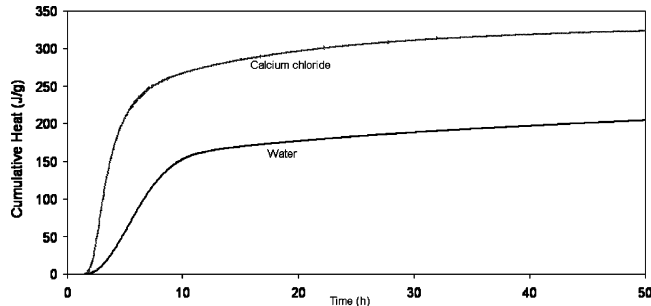
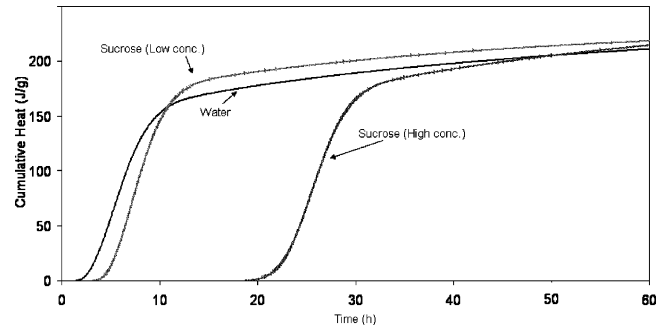
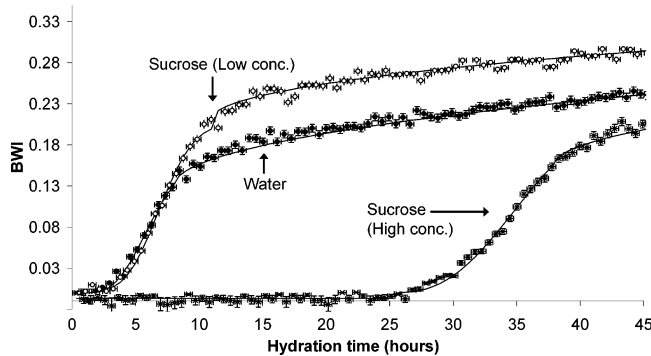
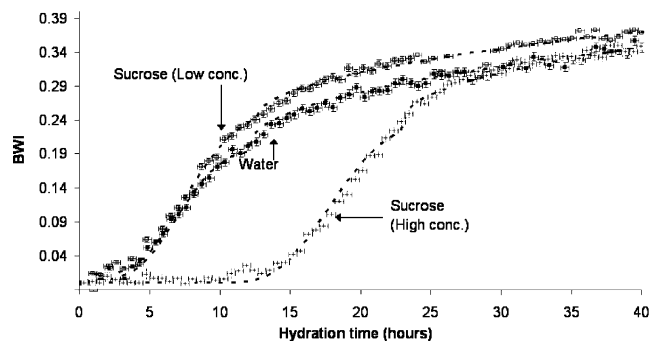
**Effects of Sucrose.** Sucrose was studied at two different concentrations. BWI versus time curves for triclinic C<sub>3</sub>S hydrated using distilled water and sucrose are shown in Figure 4 and for monoclinic C<sub>3</sub>S in Figure 5. The early data (during the induction period) show a drift in the measured value as a result of an instrumental error in the measurement of such small values for BWI (most obvious for sucrose (high concentration) in Figure 4). This error was accounted for in

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**Table 1. Parameters of the Reaction Kinetics Derived for Triclinic and Monoclinic Tricalcium Silicate Hydrated Using Distilled Water and CaCl<sub>2</sub>; Errors Are 1 Standard Deviation**

	A	d(BWI)/dt (h <sup>-1</sup> )	k (h <sup>-1</sup> )	D <sub>i</sub> (×10 <sup>-15</sup> m <sup>2</sup> h <sup>-1</sup> )	t <sub>i</sub> (h)	t <sub>d</sub> (h)	nucleation and growth duration (h)
triclinic + H <sub>2</sub> O	0.155(2)	0.022(1)	0.19(2)	0.60(3)	1.3(1)	7.9(1)	6.6(1)
triclinic + CaCl <sub>2</sub>	0.323(6)	0.089(5)	0.35(1)	5.0(5)	0.7(1)	5.2(1)	4.5(1)
monoclinic + H <sub>2</sub> O	0.193(5)	0.020(1)	0.16(1)	19(2)	1.6(1)	12.0(1)	10.5(1)
monoclinic + CaCl <sub>2</sub>	0.299(6)	0.074(4)	0.30(1)	90(9)	0.4(1)	5.3(1)	4.9(1)

**Figure 3.** Calorimetry data for triclinic tricalcium silicate pastes hydrated using distilled water and CaCl<sub>2</sub>.**Figure 6.** Calorimetry data for triclinic tricalcium silicate pastes hydrated using distilled water and 0.03 and 0.1% mass fraction sucrose solutions.**Figure 4.** BWI data for triclinic tricalcium silicate pastes hydrated using distilled water (●) and 0.0257(6)% (○) and 0.1092(6)% (×) mass fraction sucrose solutions. Dotted lines indicate the fits of the hydration models to the data. Error bars represent absolute error.**Figure 5.** BWI data for monoclinic tricalcium silicate pastes hydrated using distilled water (■) and 0.0257(6)% (□) and 0.1092(6)% (+) mass fraction sucrose solutions. Dotted lines indicate the fits of the hydration models to the data. Error bars represent absolute error.

the error analysis as represented by the averaged drift. At later times, when the BWI becomes measurably larger, this error does not contribute significantly to the overall error.

Calorimetry data for triclinic C<sub>3</sub>S hydrated with water and two concentrations of sucrose, shown in Figure 6, is in agreement with the general trends of the QENS BWI data. There is a significant difference in the measured quantities

at the end of the nucleation and growth period. This effect is particularly marked for the C<sub>3</sub>S hydrated in the presence of a low concentration of sucrose. This observation suggests a dramatic increase in the constrained H when sucrose is present. The constrained H component of QENS spectra for hydrating C<sub>3</sub>S pastes is associated with high surface area C–S–H.<sup>22</sup> This is consistent with the literature observations of an increase of surface area and microstructure of C–S–H of cement pastes hydrated in the presence of sucrose.<sup>4,5</sup>

Parameters of the reaction kinetics are compared in Table 2. As expected, the retardation (as measured by the time for set to begin, t<sub>i</sub>) increases with increasing sucrose added. A larger effect occurs for the triclinic than for the monoclinic, which is retarded only using the higher sucrose concentration. This result is consistent with the previous observation of a lower reactivity of the monoclinic, relative to the triclinic, form.<sup>15</sup> Sucrose also increases the nucleation and growth period (t<sub>d</sub> – t<sub>i</sub>), an effect attributed here to the solubilization of the silicate species caused by the sucrose.<sup>10,11</sup>

More hydration product (A) is predicted by the nucleation and growth model for both C<sub>3</sub>S forms hydrated with sucrose solutions than those with water, a result arising from the increase in the duration of the nucleation and growth period. For the monoclinic case, the values of A are in agreement for predictions using data for both sucrose solutions, indicating that the amount of hydration may have reached a maximum. This result is consistent with the results of Juenger and Jennings who identified a higher degree of hydration for portland cement after 1 year with use of a sucrose solution than with water alone.<sup>4</sup> Figure 4 shows a clear increase in the amount of reaction product produced up to 60 h by triclinic C<sub>3</sub>S hydrated with sucrose solutions, compared with that hydrated with water alone. This same monoclinic C<sub>3</sub>S sample was previously found to produce significantly more reaction product than the triclinic form; hence, the addition of sucrose did not induce such a significant increase in the amount of product formed (Figure 4).<sup>15</sup>

**Table 2. Parameters of the Reaction Kinetics Derived for Triclinic and Monoclinic Tricalcium Silicate Hydrated Using Distilled Water and Sucrose; Errors Are 1 Standard Deviation**

	A	$d(\text{BWI})/dt$ ( $\text{h}^{-1}$ )	$k$ ( $\text{h}^{-1}$ )	$D_i$ ( $\times 10^{-15} \text{m}^2 \text{h}^{-1}$ )	$t_i$ (h)	$t_d$ (h)	nucleation and growth duration (h)
triclinic + H <sub>2</sub> O	0.155(2)	0.022(1)	0.19(2)	0.60(3)	1.3(1)	7.9(1)	6.6(1)
triclinic + 0.0257(4)% sucrose	0.201(4)	0.030(2)	0.18(1)	0.40(5)	2.2(1)	11.0(1)	8.8(1)
triclinic + 0.1092(4)% sucrose	0.212(4)	0.020(1)	0.08(1)	0.48(6)	25.2(1)	37.8(1)	12.6(1)
monoclinic + H <sub>2</sub> O	0.193(5)	0.020(1)	0.16(1)	19(2)	1.6(1)	12.0(1)	10.5(1)
monoclinic + 0.0257(4)% sucrose	0.238(5)	0.025(1)	0.14(1)	16(2)	1.5(1)	12.5(1)	11.0(1)
monoclinic + 0.1092(4)% sucrose	0.240(5)	0.023(1)	0.12(1)	1.5(2)	10.8(1)	22.9(1)	12.1(1)

The nucleation and growth rate constant,  $k$ , reduces in the presence of sucrose and the increase in the nucleation and growth regime is attributed to the resulting longer time to diffusion-limited hydration. It is postulated here that after the C–S–H begins to nucleate, the sucrose still poisons many nucleation and growth surfaces. This hypothesis is consistent with the decrease in  $k$  commensurate with sucrose concentration. This work fuels the theory that sucrose is poisoning nucleation and growth sites, rather than the C<sub>3</sub>S as reviewed by Young.<sup>8</sup>

$d(\text{BWI})/dt$  increases when C<sub>3</sub>S is hydrated using the lower sucrose concentration. The higher sucrose concentration induces little effect on  $d(\text{BWI})/dt$  in the triclinic case, but in the monoclinic case  $d(\text{BWI})/dt$  increases, although not as much as is observed using the lower sucrose concentration. The  $d(\text{BWI})/dt$  represents both the rate constant ( $k$ ) and the volume of hydrating material, with its maximum proportional to the product  $Akn$ . Hence, trends for the appearance of product with sucrose do not necessarily follow the trends for the reactivity of the hydration process, as reflected by the rate constant. Sucrose has been termed a “delayed accelerant” of cement based on the observation, using microscopy, of the fast growth of hydration product in the presence of sucrose after a longer induction period.<sup>5</sup> The increase in  $d(\text{BWI})/dt$  at lower concentrations is consistent with these literature observations. The change in the rate of formation of products caused by sucrose (an increase when the lower concentration of sucrose is used) is attributed to the interplay of the reduction in the rate constant (commensurate with sucrose concentration) and the solubilization of the silicate species.

Sucrose causes a change in  $D_i$  for both forms of C<sub>3</sub>S, indicating that sucrose has an effect on the permeability of the hydration product, confirming the observation by microscopy and surface area measurements of microstructural changes to the C–S–H in the presence of sucrose.<sup>4,5</sup> The effect of sucrose decreases the  $D_i$  value for the two forms of C<sub>3</sub>S. These triclinic and monoclinic forms have been previously noted to have hydration products of significantly different permeability.<sup>15</sup>

The mechanisms of sucrose retardation are varied and unresolved in the literature. This work is consistent with solubilization of the silicate species<sup>10–12</sup> and the formation of a half-salt that poisons Ca(OH)<sub>2</sub> surfaces.<sup>8,10–12,14</sup> These results prove observations of greater overall hydration in the presence of sucrose.<sup>5,12</sup> The “delayed accelerator” phenomenon is explained by two effects: The first is an increase in the quantity of hydration products caused by a longer nucleation and growth period, postulated to arise from

continued poisoning of nucleation and growth sites. The second is an increase in the rate of nucleation and growth of products at low sucrose concentrations, postulated to arise from an increase in silicate species in solution, an effect that becomes insignificant at higher concentrations due to the reduction in the rate constant, commensurate with sucrose concentration.

#### 4. Conclusions

The hydration of C<sub>3</sub>S with water, sucrose, and CaCl<sub>2</sub> solutions was studied using quasielastic neutron scattering and calorimetry. Both sucrose and CaCl<sub>2</sub> were established to retard and accelerate, respectively, the time for set to begin of C<sub>3</sub>S. The rate constant during nucleation and growth was increased by CaCl<sub>2</sub> and decreased by sucrose; effects reflected by corresponding decreases and increases in the duration of the nucleation and growth period were induced by CaCl<sub>2</sub> and sucrose, respectively. The extent of these expected effects was commensurate with the concentration of sucrose added. Other unexpected effects on the hydration kinetics and type of hydration product were observed, particularly in the case of sucrose.

CaCl<sub>2</sub> increased the amount of total hydration product formed during early hydration, which reinforces some observations in the literature. The elimination of the differences in crystal form as the controlling factor in the reaction kinetics upon addition of CaCl<sub>2</sub> was a surprising new finding. A C–S–H phase in which the water was loosely incorporated was found to form. An increase in the permeability of the hydration products was also noted, which contributes to the increased rate constant. Some current hypotheses for the acceleration mechanism of CaCl<sub>2</sub> were supported by further effects on the hydration kinetics observed here and are thought to arise from a combined electrochemical effect of the Ca<sup>2+</sup> and Cl<sup>−</sup>, which may contribute to increased C–S–H flocculation resulting in an increased mean pore diameter.

The description of sucrose as a “delayed accelerant” in the literature was determined to arise from an increase in the rate of formation of products, although the rate constant was decreased by the sucrose. This effect is attributed to the solubilization of silicate species by the sucrose. Also attributed to the solubilization is an increase in the amount of early hydration product, although this increase is limited. Structural changes to the C–S–H were found, and a C–S–H phase in which the water was loosely incorporated was formed. The kinetic parameters indicate a decrease in the permeability of the hydration products. It is thought that the process of product formation is controlled predominantly

by the sucrose. These results are consistent with previous observation of microstructural changes, observed here by the increase in a second morphological C-S-H observed only by QENS and not by calorimetry. While these results support the leading hypothesis for the retardation mechanism, a process involving the poisoning of nucleation and growth sites, it is postulated that the solubilization of species by the sucrose plays a major role in controlling the kinetics, with

particular respect to the increased rate of formation of products, termed "delayed acceleration".

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