Tricalcium Silicate Hydration Studied using Quasielastic Neutron Scattering: Insights on the Effects of Sucrose

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1.0 Abstract

The effects of sucrose on the hydration of tricalcium silicate were studied using quasielastic neutron scattering (QENS) and calorimetry. Aside from retarding the time to set, other effects of sucrose revealed include a decrease in the nucleation and growth reaction rate and increases in the amount of early hydration product formed. These effects are discussed in terms of reaction kinetics determined by hydration modeling using QENS data. Previous literature descriptions of sucrose as a "delayed accelerant" are explained and attributed to the solubilization of the silicate species by the sucrose.

2.0 Introduction

A retarding admixture retards the setting time for hydrating cement [1]. Although it is recognized that many types of sugars, including sucrose, achieve this, there are many other effects on the hydration reported in the literature. In this paper we describe the effects of sucrose on the hydration mechanics and products from hydrating cement and tricalcium silicate. We present results from neutron scattering and calorimetry studies on the modifications to the hydration of tricalcium silicate induced by the addition of sucrose.

Sucrose has been shown to alter the microstructure and morphology of the calcium-silicate-hydrate (C-S-H) that forms from hydrating tricalcium silicate (C_3S), resulting in alteration to the bulk properties of the material [2-3]; an alteration to the hydration mechanics was implied [2]. Remarkably, sucrose has been reported to increase the rate of reaction once it had begun [2-4]. The effects of sucrose reported in the literature are not always in agreement. For example, Odler and Cordes used secondary neurals mass spectrometry to observe the effects of a 0.7 % mass fraction sucrose solution on the hydration of C_3S in dilute water suspensions and noted only a retardation of the overall hydration with no noticeable effects on the characteristics of the process [5].

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It is universally accepted that sucrose retards, in some way, the setting of cement and that this action occurs primarily through retardation of C_3S [6]. There are many theories on the retardation mechanism of sucrose.
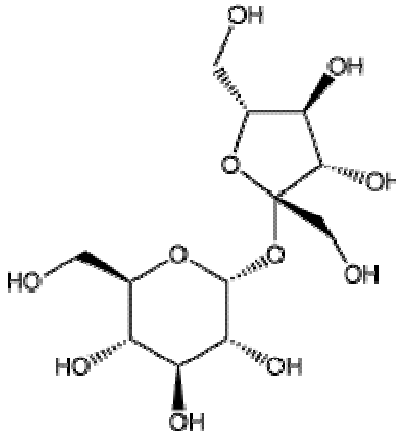

Figure1: Structural representation of sucrose

The structure of sucrose (Fig. 1) allows it to have, amongst possible interactions with C_3S paste, adsorptive properties. A hypothesized mechanism for the retardation by sucrose is the formation of a half-salt that poisons $Ca(OH)_2$ surfaces, disallowing $Ca(OH)_2$ as a nucleation site [4,6,7-8]. Sucrose is non-reducing, contains a five-membered ring, and is intermediate in its ability to form this half-salt, but stable enough not to undergo ring-opening and degradation in the alkaline C_3S paste [7].

Sucrose can chelate with Ca^{2+} [6,9] and it has been concluded from the depression of solution Ca^{2+} that the reaction kinetics were being affected [6]. It has been suggested that the preferential sequestration of Ca^{2+} affects the chemistry of the C-S-H precipitation [10]. Sucrose is also effective at solubilizing silicate in hydrating C_3S [7-8,11]. All these capabilities are consistent with, although do not explain fully, the observation of a higher rate and degree of gelation [8] and the description of sucrose as a "delayed accelerant" due to increased reaction observed by appearance of products [2-3] and disappearance of C_3S [4].

The aim of this research was to use calorimetry and modelling of quasi-elastic neutron scattering data using specific kinetic parameters to characterise the effects of sucrose on hydrating C_3S.

Quasi-elastic neutron scattering (QENS) is a useful tool in the investigation of hydration processes in hydrating cement and C_3S [12-22]. QENS spectra, $S(Q,\omega)$, are dependent on the magnitude of the scattering vector, Q, where $Q = (4\pi/\lambda)\sin(\theta/2)$, θ is the scattering angle, and the energy transfer $= \hbar\omega$, $\hbar = h/2\pi$ (h is Planck's constant). In the study of C_3S pastes the QENS spectra are dominated by the incoherent scattering

from the hydrogen, present initially in the free water and later in other states within the hydration products. QENS measures the hydrogen in all these states, including chemically bound H, constrained H, and free H, and these are able to be derived quantitatively at any time during the course of hydration.

Quantitative information about the reaction kinetics can be derived through the application of hydration models to the QENS data. Furthermore, the permeability of the products that form can be inferred. Many studies of the effects of retarders rely on calorimetry to evaluate the effects on hydration. Calorimetry is a good method for examining the rate of reaction, but cannot provide information to the depth that QENS does. The study of C_3S hydration by QENS has been previously compared to that using calorimetry [18]. Calorimetry measures evolved heat, determined in C_3S paste to be directly related to the chemical binding of H as measured by QENS. The chemically bound H component observed by QENS is associated with the formation of all the $Ca(OH)_2$ and some of the C-S-H. The constrained H is found in interlayer water in the smallest pores and adsorbed onto surfaces [18]. The constrained H as measured by QENS is associated with the formation of a high surface area C-S-H phase [18]. Evidence for two different C-S-H morphologies has been found using QENS: the chemically bound H (H_S) contributing to a phase of structure $C_{1.7}SH_{S1.6}$, and the sum of the constrained and chemically bound H (H_T) contributing to the phase $C_{1.7}SH_{T2.7}$ [18].

Here QENS is applied using a previous method [12,14-15] to investigate the effects of sucrose on the hydration of C_3S, allowing a description of the reaction kinetics and product permeability. The alterations to the hydration mechanics are quantitatively determined using terms of specific kinetic parameters, rather than simple overall hydration rates. Complementary calorimetry data using identically prepared pastes were collected and are compared to the QENS results. The results are compared to current theories for the retardation of C_3S by sucrose and hypotheses for the alterations to the hydration mechanics are presented based on extensions of these theories. The literature observation of an accelerated overall hydration caused by sucrose is resolved by this research.

3.0 Methods

3.1 C_3S and hydration solutions

Triclinic C_3S was obtained from Construction Technology Laboratories (CTL, Skokie, IL, USA). Pure sucrose was obtained from Fisher Scientific (USA), and 0.0257(6) and 0.1092(6) % mass fraction solutions were prepared using distilled water. C_3S was hydrated at 30 °C using distilled

water and the sucrose solutions, using a fluid to component mass ratio of 0.4.

3.2 QENS

QENS measurements were carried out using the NIST Center for Neutron Research neutron time-of-flight Fermi Chopper Spectrometer (FCS) [23]. C_3S pastes were sealed in a Teflon insert (approximately 0.5 mm thick) inside a rectangular aluminum can, which was placed at a 45 ° angle to the incident neutron beam. Each energy-transfer spectrum was 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 summed from several detectors corresponding to the Q range 2.0-2.3 $Å^{-1}$. QENS data collection commenced approximately 30 minutes after initial mixing, data were collected continuously for up to 55 hours and time-averaged over 33 minute intervals. The incident neutron wavelength used was 4.8 Å. The energy resolution at the elastic line, ΔE, is 0.146 meV.

The kinetics of the hydration reaction were characterized using the "Bound Water Index" (BWI) which represents the ratio of less mobile H (sum of the chemically bound and constrained H) relative to the total H in the system. The BWI is representative of the amount of product and was derived with respect to time during the course of hydration. Using the time dependent BWI curves, two models were applied: 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, enabling the derivation of parameters describing the kinetics of the hydration reactions. These exact methods of QENS analyses and hydration modeling have been reported elsewhere [12,14-15].

The kinetic parameters derived were 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 mechanics had not been interrupted. These parameters have been shown to correlate to physical properties of the paste. The parameter t_i is also the time at which setting begins. D_i is related to the permeability of the hydration layer around the hydrating C_3S grains [17] and can be used as an indicator for morphological and microstructural changes to the hydration product. The parameter A is independent of the type of product that is formed and is useful for predicting how much hydration will initially occur, correlating with early strength.

3.3 Calorimetry

Calorimetry measurements were carried out using the TAM Air heat flow calorimeter (Thermometric). Hydration took place at 30 °C inside sealed 20 ml glass ampoules using approximately 5-7 g samples. Data were collected continuously for 50 hours and the cumulative heat evolved per gram of C_3S was derived with respect to time.

4.0 Results and discussion

As the chemically bound H component matches the cumulative heat evolved, the QENS data contain the same measured quantities as the calorimetry data and additional information about reaction products that incorporate constrained H, whose formation is not associated with the evolution of heat at this time [18]. The QENS data are therefore used to measure the changes to the reaction kinetics, whilst comparisons between the QENS and calorimetry data allow dissemination of the type of C-S-H.

BWI versus time curves for C_3S hydrated using distilled water and sucrose are shown in Fig. 2 and calorimetry data are shown in Fig. 3.
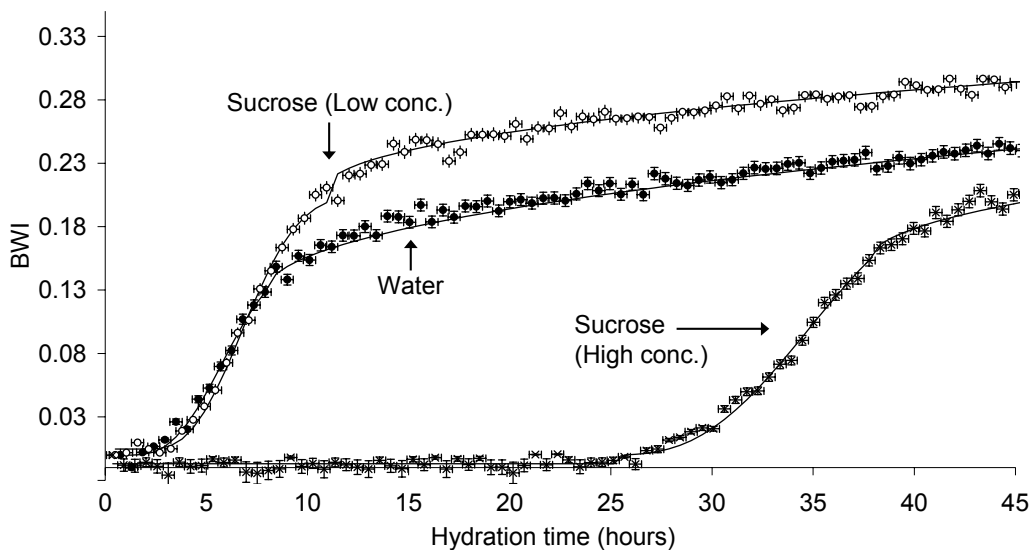

Figure 2: Time dependent plot of the Bound Water Index obtained from quasielastic neutron scattering of hydrating tricalcium silicate with various amounts of sucrose. The lines through the data represent the output from the kinetic models for the data.
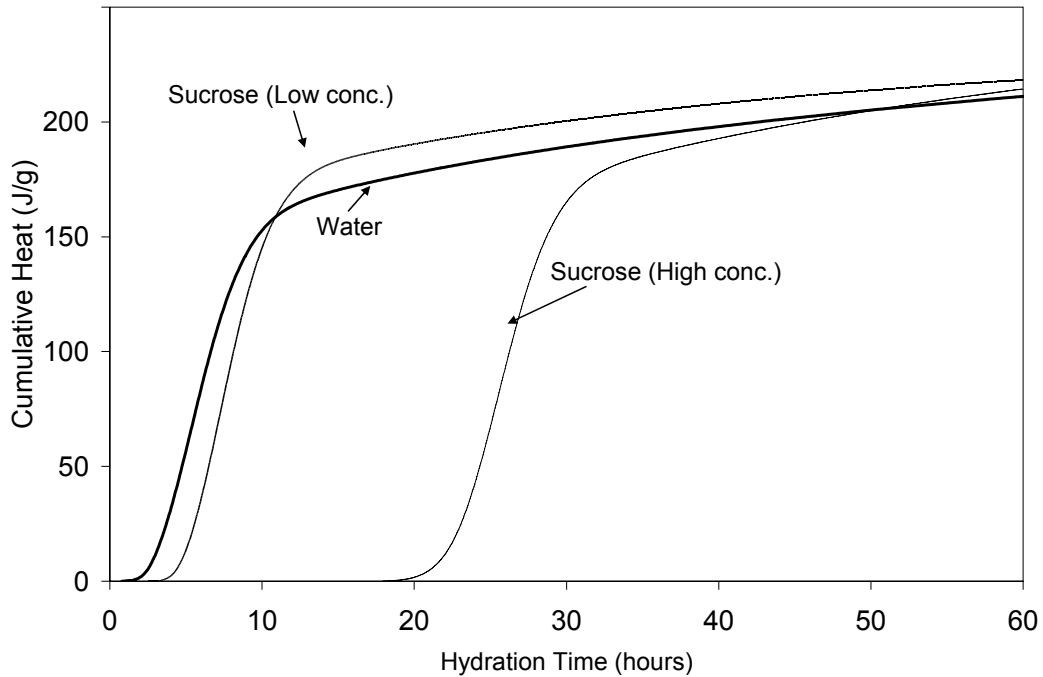
Figure 3: Time dependent plot of the cumulative heat evolution obtained from calorimetry data of hydrating tricalcium silicate with various amounts of sucrose. Error in y is 1.5 % and not shown for clarity.

Whilst the trends of the hydration behavior shown in these two figures agree, there is a significant difference in the measured quantities of hydration products of sucrose samples relative to the hydrated sample at the end of the nucleation and growth period. This is illustrated in Table 1, which lists the composition in terms of the percentage of H in each state present at 45 hours hydration, after the nucleation and growth period ends. The greater separation in hydration products observed by QENS relative to the cumulative heat evolved suggests a dramatic increase in the constrained H when sucrose is present. The constrained H component of QENS spectra for hydrating C_3S pastes is associated with high-surface area C-S-H [17]. 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 [2-3].

Table 1: Composition of tricalcium silicate hydrated with various amounts of sucrose as the state of hydrogen.

% mass fraction sucrose ↓	Structural H (%)	Constrained H (%)	Free H (%)	Structural and Constrained H (%)	Cumulative heat evolved (J/g)
0	19.5(2)	7.9(5)	72.6(7)	27.5(6)	202(3)
0.0257(4)	22.0(2)	10.2(7)	67.8(7)	32.2(6)	211(3)
0.1092(4)	17.1(2)	7.3(4)	75.7(8)	24.4(5)	199(3)

Parameters of the reaction kinetics are compared in Table 2. The parameters t_i, t_d, and A increase whilst k and D_i decrease, upon addition of sucrose. The effect of sucrose on the rate of formation of products during product nucleation and growth, d(BWI)/dt, was dependent on the sucrose concentration.

Table 2: Kinetic parameters for tricalcium silicate hydrated with various amounts of sucrose derived from quasielastic neutron scattering data.

% mass fraction sucrose ↓	t_i (h)	t_d (h)	Nuc. and Grow. duration	A	d(BWI)/dt (h^{-1})	k (h^{-1})	D_i (x 10^{-16} m^2h^{-1})
0	1.3 (1)	7.9(1)	6.6(1)	0.155(2)	0.022(1)	0.19(1)	6.0(3)
0.0257(4)	2.2(1)	11.0(1)	8.8(1)	0.201(4)	0.030(2)	0.18(1)	4.0(5)
0.1092(4)	25.2(1)	37.8(1)	12.6(1)	0.212(4)	0.020(1)	0.08(1)	4.8(6)

As expected, the retardation (as measured by the time for set to begin, t_i) increases with increasing sucrose concentration. Sucrose delays the onset of diffusion limited hydration resulting in an increase in the duration of nucleation and growth of products, represented by t_d-t_i. This increase is attributed here to an increase in the quantity of silicate in solution arising from the solubilization of the silicate species caused by the sucrose [7-8].

Fig. 2 shows a clear increase in the amount of reaction product produced up to 45 hours by C_3S hydrated using sucrose solutions, compared with that hydrated using water alone. This is reflected in the parameter A, which predicts that more hydration product will form from the nucleation and growth processes for C_3S hydrated using sucrose than for water. This result arises from the increase in the duration of the nucleation and growth period and is consistent with previous observations of a higher degree of hydration for portland cement after one year using sucrose [2]. The increases in the amount of hydration product formed from C_3S hydrated with sucrose confirms previous observations of greater overall hydration in the presence of sucrose [3-4], hypothesized to occur through an increase on silicate species in solution, explaining its "delayed accelerator" effect.

The nucleation and growth rate constant, k, reduces in the presence of sucrose. It is postulated here that after the C-S-H begins to nucleate, the sucrose continues to poison many nucleation and growth surfaces. This hypothesis is consistent with a decrease in k commensurate with sucrose concentration. This work fuels theory that sucrose is poisoning nucleation and growth sites, rather than the C_3S as reviewed by Young [6].

d(BWI)/dt is the rate of formation of products during the nucleation and growth regime, and differs from k as the d(BWI)/dt represents both the rate constant (k) and the volume of hydrating material. Trends for the rate of appearance of product during the nucleation and growth period, d(BWI)/dt, do not necessarily follow the trends for the reactivity of the

hydration process, as reflected by the rate constant, k. d(BWI)/dt increases when C_3S is hydrated using the lower sucrose concentration, whilst the higher sucrose concentration induces little effect on d(BWI)/dt. The "delayed accelerant" effect of sucrose [2-4] is consistent with the increase in d(BWI)/dt at lower concentrations. The increase in the rate of formation of products using the lower concentrated sucrose solution is attributed to the interplay of the reduction in the rate constant (k) commensurate with sucrose concentration and the solubilization of the silicate species that contribute to an increase in the quantity of silicate ions in solution available to form products. Although sucrose is able to chelate Ca^{2+}, the solution remains saturated with respect to Ca^{2+} [7].

Given the increase in the constrained H when sucrose is present, associated with high-surface area C-S-H and the literature observations of an increase of surface area of C-S-H of cement pastes hydrated in the presence of sucrose [2-3], a change in the permeability of the products during diffusion limited hydration is expected. Sucrose induces only a small decrease in permeability, as indicated by the D_i, suggesting that the previously observed changes to the microstructure [2-3] are linked to the development of the C-S-H phase in which water is loosely incorporated.

This work adds clarity to the mechanisms for retardation of C_3S by sucrose, which are varied and unresolved in the literature. The results of this work are consistent with solubilization of the silicate species [7-8,11] and the formation of a half-salt that poisons $Ca(OH)_2$ surfaces [4,6,7-8,11].

5.0 Conclusions

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 during nucleation and growth, although the reaction constant during this period was decreased by the sucrose. This effect is attributed to the solubilization of silicate species by the sucrose. Also arising from the solubilization is an increase in the amount of early hydration product.

Structural changes to the C-S-H were found, in particular a C-S-H phase in which the water was loosely incorporated was formed. These results are consistent with previous observation of microstructural changes, observed here by the increase in a C-S-H phase observed only by QENS and not by calorimetry.

Whilst these results support the leading hypothesis for the retardation mechanism, a process involving the poisoning of nucleation and growth sites, it is shown here 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".

6.0 References

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