The Role of Water during Setting and Hardening of Tricalcium Silicate Paste

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Abstract

Deuterium NMR has been used to track the T_1 relaxation times of deuterons in hydrating tricalcium silicate (C_3S) pastes held at 23°C. Deuterated water was used to facilitate NMR measurements. T_1 times gathered as a function of time were correlated with corresponding Vicat needle and isothermal calorimetry data. To date it has been universally accepted that the growth of layer-like C-S-H during the acceleratory period was the cause of both the relatively large evolution of heat that takes place as well as the cause of setting and hardening. A new paradigm for setting of C_3S paste is proposed based in part on previous T_1 studies of kanemite and zeolite A and in part on T_1 data reported here. Due to the fact that T_1 times decrease from ~400 ms (liquid state) to ~10 ms (solid state), it is suggested that initial setting of C_3S paste is initiated by the formation of bridges of solid state water (4-5 molecular layers thick) that form between adjacent C-S-H foils. As the growth rate of C-S-H increases, water filled pores become increasingly populated with hydrates. Relative spacing between adjacent foils decreases, which causes the formation of increasingly larger numbers of solid state water bridges. The rate of heat evolution, hydrate surface area and connectivity increase, the paste becomes more viscous and firmer and finally it sets (no Vicat needle penetration). Solid water bridges are composed of hydrogen/covalent bonded arrays of tetrahedrally coordinated oxygen atoms. The open oxygen network of these arrays allows for Ca^{2+} and SiO_4^{4-} diffusion causing the solid water bridges to change into C-S-H with time.

1. Introduction

The kinetics and microstructural evolution of hydrating tricalcium silicate (Ca_3SiO_5) is studied by cement chemists in order to gain insight into the synergistic physical and chemical processes taking place during the setting and hardening of these pastes. A second but less rigorous reason for studying a simplified model system is based on the assumption that reactions observed in the simple system can be used to explain similar but more complex reactions taking place in the much larger system known as

hydrating Portland cement. That is to say, the systems are chemically different, yet they do seem to have parallel sequences of reaction.

Tricalcium silicate (C_3S) is the major component in Portland cement as well as the primary source of calcium and silica needed to form calcium silicate hydrate (C-S-H), the major strength producing phase in hydrated Portland cement and concrete. The use of C_3S as a model system for hydration studies has a long history. C_3S mixed with water (paste) has been studied for ~100 years and continues to be studied as new techniques are developed and new students try to grasp the underpinnings of the hydration process. It has been the goal of researchers to explain the relation of microstructure and chemistry during the evolutionary process known as setting and hardening. It has been the hope of each generation to fully understand the process and then use this knowledge to design a more durable Portland cement and concrete.

The research presented here falls into this same category. Solid state NMR has been used to obtain classical powder patterns and deuterium T_1 relaxation times for C_3S mixed with deuterated water (D_2O). The T_1 data were correlated with companion Vicat needle, calorimetric and morphological data as a means of confirming a potential phase change from liquid to solid state water during initial setting and hardening.

Early studies, such as those of Flint and Wells [1] and Roller and Ervin [2] generally focused on delineating the chemistry of the solution phase in equilibrium with various combinations of lime and silica mixed with water. Although the work was groundbreaking, it left many questions about the nature of the solid phases unanswered. Once Kondo and Ueda [3] demonstrated that isothermal calorimetry could be used to track heat evolution as a function of reaction time, the research community began to realize that the hydration process was far more complex than they had imagined. Researchers began to initiate studies that, to a greater extent emphasized the crystal chemistry, kinetics and microstructure of the solid hydrates that were forming.

It became clear that something odd was happening. Tricalcium silicate and Portland cement mixed with water had an induction period. The cause of this "inactivity" or dormancy makes it possible to mix and place Portland cement paste before it sets, but it also adds a complexity to the modeling process that has not yet been fully resolved. If the processes prior to and during the induction period are ignored for the moment, calorimetric plots for C_3S pastes indicate that the dormancy period is followed by a so called acceleratory period during which large amounts of heat are given off, the cement sets and then hardens. This process normally occurs 4-5 hours after mixing and continues for 18-24 hours [3]. During this time period the solution composition changes dramatically [4,5] as C-S-H and $Ca(OH)_2$

precipitate and form growing networks of interlocking foils interspersed with larger $Ca(OH)_2$ crystals [6].

2. Models

A hydration model that has stood the test of time is one originally proposed by Taylor. His model and modifications thereof generally deal with the structure and composition of the phases that form during and long after the acceleratory period. The phases that form within a few minutes of mixing and their causative role in initiating the induction period are generally not discussed in detail. Although there is a burst of heat during the first 15 minutes after mixing [3], subsequent heat evolution typically decreases to very low values for the next 4-6 hours as active dissolution, precipitation and growth slow and reactions come to a halt. ESCA data for the first few minutes of C_3S hydration [8-11] suggest that the surface of the C_3S undergoes an almost immediate transition from Ca-rich to Ca-poor and then back again to Ca-rich in a matter of 15 minutes or so. What ever is happening causes the solid C_3S in the system to become inactive (i.e. become nearly insoluble). Various theories (most often evoking some type of barrier layer) have been put forth, but the related issues of what causes the barrier layer and what causes it to end are still not fully resolved. There is however almost universal agreement that once the induction period ends, there is a resurgence of chemical activity, a layer structured C-S-H having a tobermorite/jennite-like structure and $Ca(OH)_2$ crystals nucleate, grow and interlock [12]. Evidence offered in support of this model are 1) the large increase in the rate of heat liberation during the early part of the induction period, and 2) the fact that the paste sets and hardens about ½ way through the induction period.

3. Objective

A model requiring physical intergrowth of foils and fibrils is troublesome for a number of reasons. The most evident being the ability of a paste to go through cycles of mixing and each time exhibit a nearly consistent yield stress followed by near Newtonian behavior (ignoring hystereses for the moment) [13]. There must be other mechanisms at work; it would seem that surfaces must somehow become attached to one another nearly instantaneously. Thus chemical bonding via C-S-H formation between foils through a water film seems unlikely, because the rates of diffusion would be relatively long. Let us instead assume that there is a certain amount of surface roughness developing on C_3S grains as hydrates grow outward and begin to populate previously water filled spaces, and that some of the C-S-H foils on adjoining C_3S grains touch each other and the liquid films on their surfaces form hydrogen bonds. This type of bonding will provide some rigidity and increase viscosity via growth of clusters and ultimately connectivity among clusters, but it is also assumed that liquid state bonds

are not strong enough to explain setting and hardening even with "explosive" C-S-H growth. It is now proposed that one or two monolayers of the water on the surfaces of the foils is in the solid state, and that bridges of solid water provides the connectivity between closely spaced foils that leads to initial setting and hardening. The suggestion that films of structurally orientated water occur between layered silicates is not a new idea. Recently it was shown that the surface of a mica flake was hydrophilic to the point that the strength of the hydrogen bonds that formed between the protons in water molecules and the lone pair electrons of the tetrahedrally coordinated oxygen atoms present on the surface (i.e. the Q_3 silicate ions) was large enough to immobilize the water molecule, i.e. large enough to cause the water to change state from liquid to solid [14]. NMR T_1 relaxation times measured for kanemite [15] and a variety of silicates [16] also suggest the existence of solid state water in these systems because deuterium T_1 times are extremely short (~10 ms).

4. Theory

It is known that water will form hydrogen bonds with oxygen networks found on the surfaces of layer silicates. The silica tetrahedra that form the surface link together to form sheet-like arrays of 2D hexagonally arranged silicate ions, i.e., in the parlance of NMR, they have Q_3 connectivity. Due to the lone pair electrons that the oxygen ions have, the protons in liquid water molecules adjacent to these surfaces will form hydrogen bonds with the oxygen on the surface. Independent studies of the nature of monolayers of water on the surface of mica [13] and kanemite [14] and sodium montmorillonite [17] indicate that at a minimum a monolayer of water on these surfaces is in the solid state-i.e. the strength of the hydrogen bonds is great enough to overcome the molecular motion of the water molecules associated with the liquid state. By definition, water molecules with dynamics that are confined to a lattice (at the atomic level) are in the solid state. Such adsorbed water is akin to the so called "zeolitic" water that one observes when one runs a TGA on clay or mica or for that matter a C-S-H sample [18]. The water comes off gradually without distinct sharp vertical weight losses as seen in $Ca(OH)_2$ or $CaSO_4 \cdot 2H_2O$ [12]. The strength of the hydrogen bond is not unlimited and at some point enough thermal energy can be supplied to the system to disrupt the bond causing the water to liquefy and evaporate. Note that the water would liquefy gradually; the water furthest from a silicate surface would be driven off first followed by more strongly bonded water closer to the silicate surface at higher temperatures.

It is proposed that the thickness of a water layer on the surface of a C-S-H foil is partially governed by the atomic-level structure of the foil (a so called templating effect) and the temperature of the hydrating system. This is conjectural at this point, but based on the fact that C-S-H has a layer-like

structure consisting of two outer silicate layers populated by rows of drierketten $[(Si_3O_9)^{2-}]_n$ that are occasionally cross linked to each other (i.e. predominantly Q_2 with a trace of Q_3 silicate ions) bounded to a central octahedraly coordinated layer of CaO, and the fact that said layer structure has similar water adsorption/desorption behavior as exhibited by zeolite and clay, it is hypothesized that solid state water should also be present on the surfaces of and in interlayer positions of C-S-H foils.

The surface of the C-S-H foil consists of a pseudo-hexagonal arrangement of oxygen atoms whose two lone pairs point outward into interlayer space. Surface morphology and charge are ideal for the formation of solid water arrays having an "ice-like" structure, i.e. water molecules form hexagonal networks of hydrogen bonded water molecules that mimic the silicate surface (i.e. the silicate surface acts like a template). The formation of hydrogen bonds with the hexagonal silicate surface imparts enough thermodynamic stability to overcome the molecular motion of the water molecules in the liquid state at temperatures well above ambient. Because of templating effects, hydrogen bonding is strongest directly at the at the silicate surface. The solid state water that forms there is the most stable relative to additional layers forming further from the silicate surface. Obviously, as more layers are added the energy of bonding will be equal to or less than that needed to cause a phase change and the outermost solid water will begin to coexist with liquid water. The thickness of the solid layer is also influenced by ions in solution that can/can not stabilize the solid state lattice. Those ions that fit into the open "ice-like" lattice will stabilize the structure. It is noteworthy that Ca^{2+} is of the right size to stabilize.

5. Experimental Methods

Conventional tools including Vicat needle, X-ray diffraction, isothermal calorimetery and SEM were used to study the kinetics of setting and hardening of C_3S + (H_2O or D_2O) pastes maintained at 23°C. In parallel with these measurements, NMR was used to collect static ^2H NMR powder patterns and T_1 relaxation times for complimentary D_2O pastes run in sealed capsules in real time at three different magnetic fields.

How does one determine if the water is in the solid state? One way is to use D_2O hydrated samples and NMR to determine relaxation times of the deuteron. In liquid D_2O T_1s are nominally in the 400 ms range at room temperature and in the extreme narrowing motional regime, independent of the magnetic field. In kanemite, zeolite A, and in the solid water fraction of hydrating cement pastes at room temperature, the T_1s are nominally in the 3-10 ms range with magnetic field dependence. In the solid state, the dynamics of the D_2O molecules (or the D nuclei) is limited to jumps on the tetrahedral lattice of the solid water, and this produces the observed 3-10

ms T_1 values. In the liquid state, D_2O molecules experience isotropic rotational diffusion, and this produces the observed 400 ms T_1 value.

Tricalcium silicate was synthesized from reagent grade silicic acid and $CaCO_3$. These were mixed in stiochiometric proportions, ball milled in absolute ethyl alcohol with alumina/zirconia balls until homogeneous (typically 24 hours). The mixture was poured into a Pyrex dish allowing the alcohol to evaporate at room temperature. The resulting powder was pressed into one inch diameter pellets, stacked on a zirconia plate and repeatedly fired (after grinding between firings) in a molydisilicide furnace at 1400-1500°C. The sample was X-rayed and found to be single phase tricalcium silicate (M_1 polymorph). No evidence of CaO was observed.

The sample was ground by hand in an agate mortar and then ball milled dry with zirconia balls. The Blaine surface area of the powder was measured as 3400 cm^2/g. The powder served as the starting material. It was mixed at one D_2O/C_3S ratio (0.40). The well mixed paste was placed in NMR sample tubes and sealed with epoxy for analysis as a function of hydration time. The NMR spectrometers used to investigate the T_1s were a Chemagnetics CMX-300, a Chemagnetics Infinity 500, a Bruker DRX-400, a Bruker DPX-300, a Bruker AMX2-500, and a Bruker DRX-600. The inversion-recovery pulse sequence was used to measure the ^2H T_1's at 3 different magnetic fields. The resulting T_1 data were fit to a monoexponential decay function and the T_1 values at the 3 different fields were used to calculate the fraction of liquid water to solid water present as a function of time based on equation (1).

$$\left(\frac{1}{T_1}\right)_{observed} = f_{liquid}\left(\frac{1}{T_1}\right)_{liquid} + f_{solid}\left(\frac{1}{T_1}\right)_{solid} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

The total fraction of water must be 1, and the T_1 liquid at all 3 fields is 400 msec. At any given time of hydration, the f_{liquid} and f_{solid} values must be fixed and independent of the magnetic field. With these stipulations, the magnetic field dependent T_1 solid values were found to converge to the same values we found for kanemite at the same temperatures [15]. This enabled us to back out the fraction of liquid to solid as a function of time.

Corresponding paste samples made with D_2O and DI water were also tested using a Vicat needle that penetrated into the paste cast into a small paste filled mold (2" in diameter and 2" tall). The mold was covered with plastic wrap to prevent evaporation in as much as setting took close to 24 hours when D_2O rather than H_2O was used to hydrate the sample. See Figure 1. Penetration gradually decreased to zero as the sample set and finally hardened. The paste was also studied using a Thermonetics isothermal conduction calorimeter maintained at 23°C for similar periods of time. In this case paste samples were mixed externally and then placed

in a square stainless steel tightly lidded/sealed sample holder that fit snugly into the calorimeter cup. Data were collected via a computer data
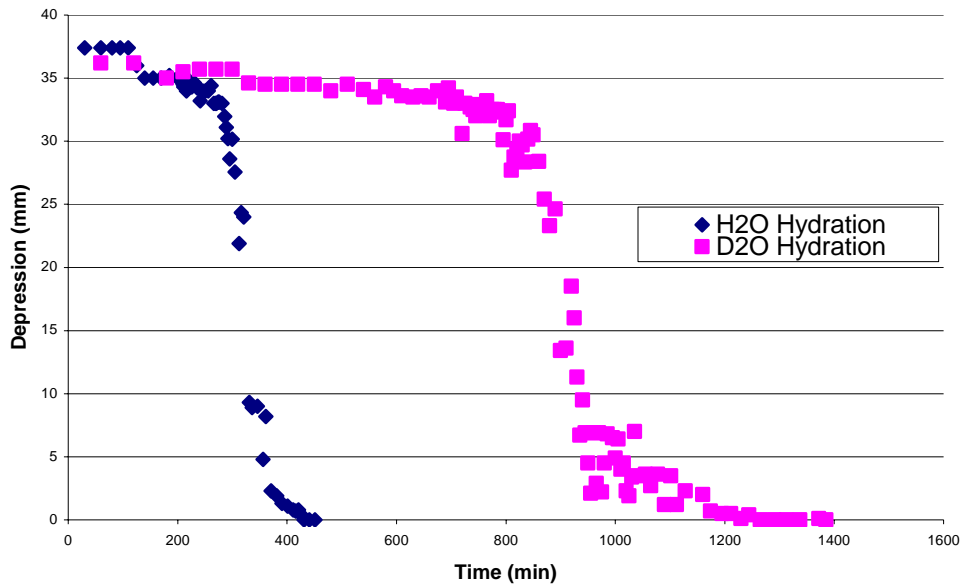
logger.

Figure 1. Vicat traces of C_3S/H_2O (w/s=0.36) versus C_3S/D_2O (w/s=0.40). Penetration times for pastes at 23°C. Times are approximately 3X as long when hydration is carried out using D_2O versus H_2O. D_2O is a retardant.

Finally, small subsamples of paste made with DI H_2O were allowed to hydrate at 23°C as a function of time in sealed glass vials. Using Vicat needle penetration for DI water mixed pastes as a sign of setting for the H_2O system, glass vial samples of the same age (w/s =0.36) were freeze dried and used to examine microstructural characteristics (SEM) as a function of time. See Figure 2 for the actual samples studied (1-8).
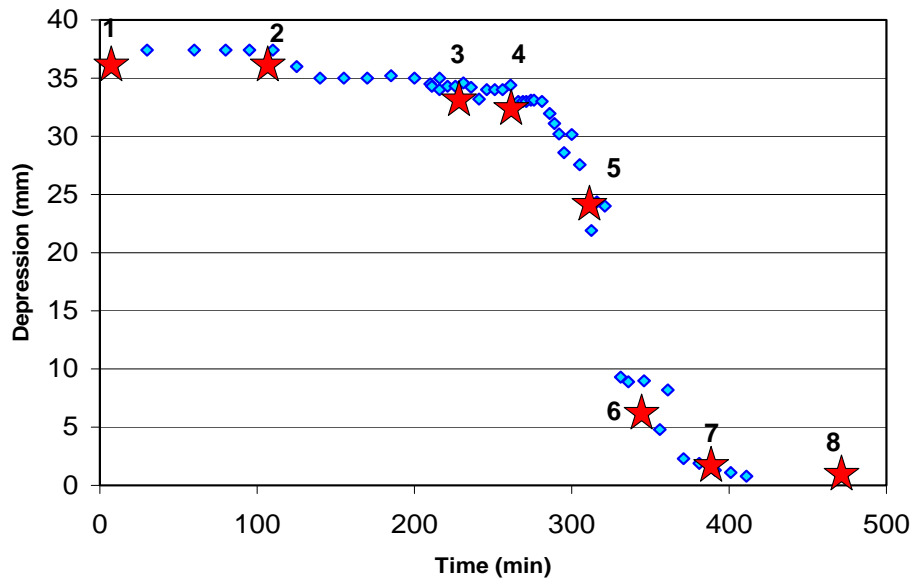
Figure 2. Vicat trace with numbered sampling points. Samples in glass vials were freeze dried to stop hydration. Hydration times are what one normally expects when hydrating C_3S with H_2O.

6 Results

A compilation of C_3S+D_2O paste data is given in Figure 3. T_1 relaxation times were measured on the same set of samples using different magnetic fields (9.39, 7.02 and 11.74 Tesla) at their Larmor frequencies. Vicat data was measured using a modified ASTM C 191 procedure using a 2'' diameter by 2'' high sample cup. Isothermal calorimetery was measured at 23°C using a Thermonetics isothermal conduction calorimeter.
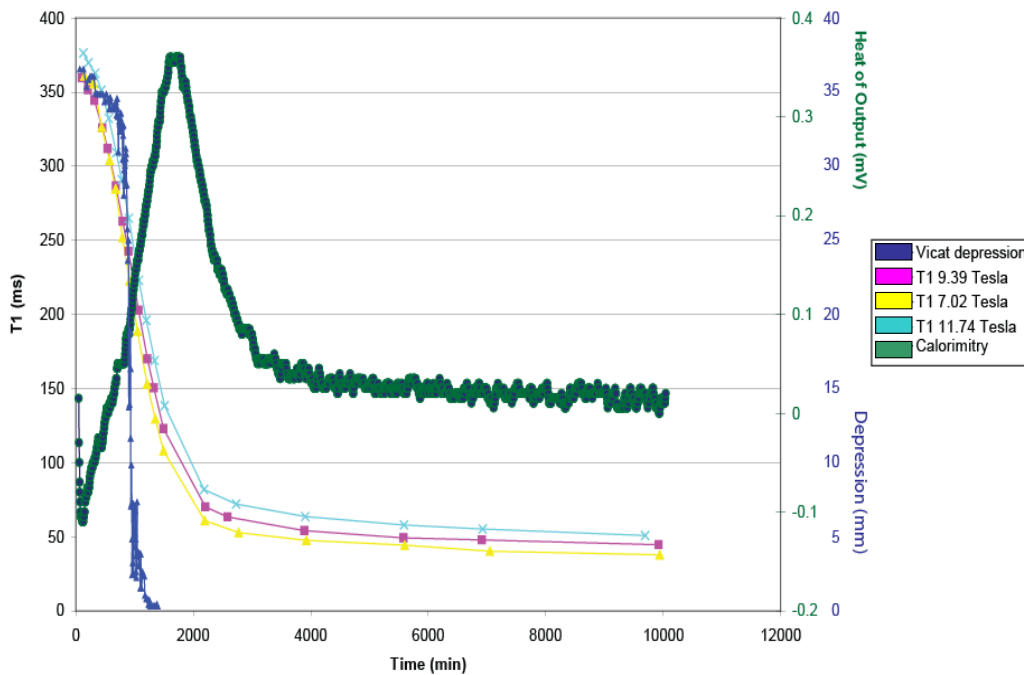
Figure 3. Data Compilation for D_2O-hydrated C_3S.

This plot contrasts the behavior of three data sets plotted on a common time axis. One can see the interrelation of penetration depth, heat flux, and T_1 relaxation times for hydrating C_3S + D_2O paste. There are major changes occurring in the paste at ~1000 minutes. The paste is thickening, it is warming and the T_1 relaxation times are falling. Collectively, these trends indicate that the paste is well on its way to becoming a solid. The new observation here is that the T_1 times are leaving the realm of liquid water and approaching those attributed to solid state water. It was observed that T_1 times decreased from a high of 400 ms (typical of liquid water) to a low of 10-40 ms (typical of solid water in restricted geometries) with time at all three frequencies measured. We believe that a few monolayers of solid water exist on all solid surfaces in the paste, but it is the solid water that covers the surfaces of nucleating and growing foils of C-S-H and $Ca(OH)_2$ crystals that is responsible for the initial joining of solid particles during the initial stages of the acceleratory period. The individual surfaces covered with solid state water eventually touch another foil and hydrogen bond together (forming bridges of solid water). These bridges comprise the initial network contacts that form at an increasing rate during the setting process. The heat evolved is thus partly due to the heat of fusion of the water and in part due to the formation of stable C-S-H and $Ca(OH)_2$ hydrates.

Microstructures of selected DI water hydrated samples are given in Figure 4. These reflect an increase in the number of foils that are seen forming on the surfaces of the C_3S grains with time. The increase in the number of foils parallels the decrease in T_1 and Vicat needle penetration depth. The heat evolution indicates that reaction rates are increasing as more foils are produced.
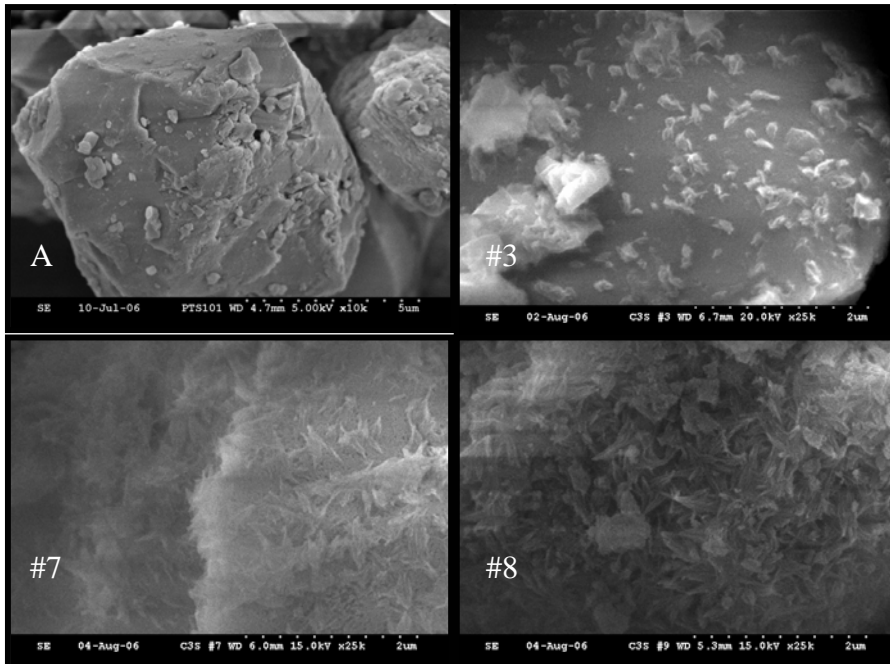
Figure 4. Microstructures of C_3S pastes. A= anhydrous. #3= 240 min. #7= 385 min. #8= 485 min. Massive foils present 385 minutes and later.

Quantative analysis of the T_1 data for D_2O containing samples hydrated for more than 80 days is presented in Figure 5. The two plots allow one to observe the amount of solid versus liquid water present in the sample at any given time. These data differ from the earlier data in as much as they cover the entire range of hydration terminating at a point in time where one might normally consider a sample of C_3S plus D_2O sample fully cured (3X 28 days) [12].

7 Conclusions

It is concluded that hydrated tricalcium silicate pastes that are beginning to set contain enough solid state water to coat growing C-S-H foils and at the same time form solid water bridges between grains that are close enough
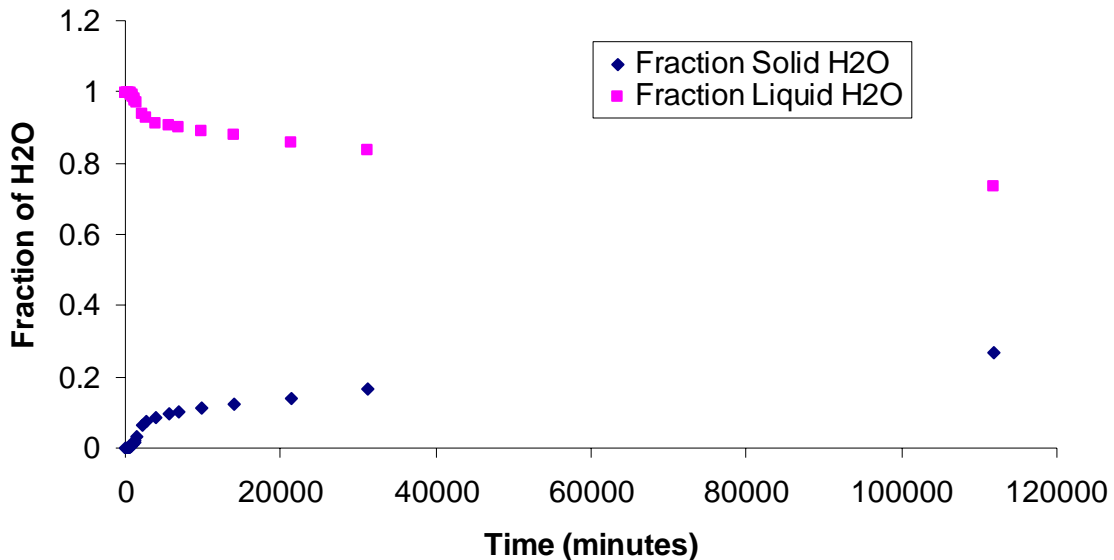

Figure 5. Quantative analysis of the T_1 data as a function of time. The fractions of liquid and solid water were calculated using Equation 1 for a C_3S +D_2O paste hydrated in a sealed SiO_2 tube.

that the solid water surfaces join together. At zero penetration the sample appears to contain roughly 10% solid water and 90% liquid water. Given the amount of surface area the sample has at this point, the solid water would form a film ~3 molecular layers thick. Also the amount of heat given off during setting is close to the amount of heat one would expect if an equivalent amount of water was frozen (a.k.a. the heat of fusion of that

amount of water could account for a similar magnitude of heat evolution). Undoubtedly, there is a certain amount of heat evolution due to the formation of C-S-H and $Ca(OH)_2$, but the free energy of formation of the compounds themselves may be too high in light of the fact that solid water could also be forming on and between adjacent surfaces.

It is suggested that the heat evolution during the acceleratory period has two sources: one is related to the chemical reaction as solid C-S-H and $Ca(OH)_2$ precipitate and grow from solution. Surface area measurements by Weiker [10] suggest that the increase in surface area due to C-S-H formation is similar to the heat evolution curve typically associated with hydrating C_3S paste. A second source of heat is the conversion of adsorbed water films to the solid state. As more silicate surfaces are formed, the molecular films of water on their surfaces are converted to the solid state.

Based upon the data and a bit of conjecture it is suggested that the initial setting one observes when C_3S pastes begin to thicken is due to the formation of solid state water bridges between foils and fibrils. There is no mechanical intergrowth of foils because each foil is covered with a molecular layer or two of solid water. What touch are these solid water surfaces. Because the initial bonds that form are hydrogen bonds and their relative numbers are small, strength is relatively low. As a result, pastes can be stirred and liquefied, but once they are allowed to rest they regain their so called Bingham liquid behavior. They have a yield stress and more or less Newtonian behavior thereafter. They are shear thinning. There is a hysteresis present in the down curve that can be accounted for by reestablishing hydrogen bonds.

When set occurs networks are more mature-there are more solid-solid water bridges as well as particle to particle contacts. Setting is due to the intergrowths of layers of solid water and ultimately the foils and fibrils themselves. The solid water on silicate surfaces in the system provide a pathway for diffusion of Ca and Si ions through the "open" tetrahedrally coordinated array of water molecules that make up solid state water.

This makes it possible to form a silicate network in situ. Ca and Si atoms can migrate through the oxide structure and form additional solid C-S-H. The deuterons in the water will migrate into the underlying C_3S to form inner product. Deuterons hop from tetrahedral site to site via Bjerrum and ionic defects [15]. If this model is correct, it may in fact begin to shed some light on the nature and state of water during setting and hardening and the cause of the associated exothermal reaction of setting cement paste.

8. References

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